

Lund Reports on Atomic Physics

DOPPLER-FREE AND TIME-RESOLVED LASER SPECTROSCOPY

FOR

HYPERFINE STRUCTURE AND LIFETIME DETERMINATIONS

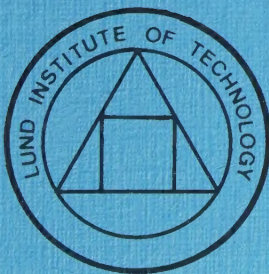
OF

EXCITED ATOMIC STATES

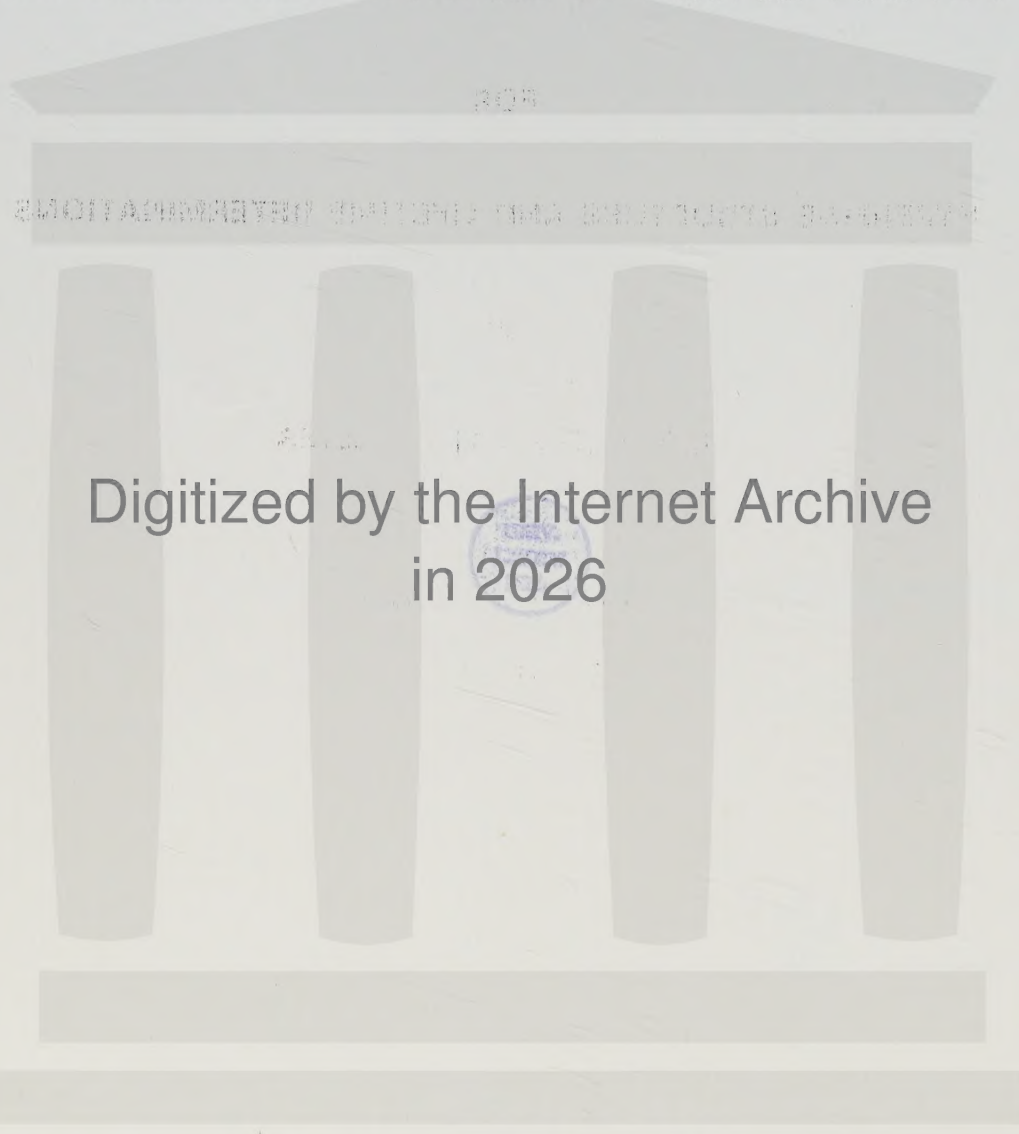
BY

STEFAN KRÖLL

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STEFAN KRÖLL

LUND JANUARY 1986

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ABSTRACT

Hyperfine structure, isotope-shift and lifetime data of excited atomic states have been obtained using Doppler-free and time-resolved laser spectroscopy.

Several different laser saturation spectroscopy techniques have been intercompared regarding their potential for Doppler-free spectroscopy in noble gases and refractory elements in a hollow cathode discharge. Velocity-changing collisions, cross-over signals, sputtering efficiency, choice of modulation frequency and other aspects of this kind of measurement situation are discussed. New hyperfine data are presented for vanadium.

New lifetime data have been obtained for Rydberg states in magnesium, aluminum and oxygen using two-step pulsed laser excitation. The fluorescence decay has been captured with a photomultiplier connected to either a transient digitizer or a box-car integrator.

The lifetimes measured in magnesium were compared with available theoretical calculations of oscillator strengths and very good agreement was obtained. The measurements were performed in a region of strong configuration interaction and the lifetimes calculated from the theoretical oscillator strengths were quite sensitive to the admixture of the interacting configurations. This shows that a fruitful interplay between theoretical calculations and lifetime measurements may be possible in low excited states.

In the measurements in oxygen, ground state oxygen atoms were produced by photodissociation of nitrogen dioxide molecules. Two-photon absorption was used in the first excitation step. In this way the large energy gap between the ground state and the excited states could be bridged for this light element. A similar approach can be used to reach excited states in other light elements where hyperfine structure and lifetime data today are scarce. A simple rate equation approach was used to estimate the population in the upper state after the photodissociation and two-photon absorption processes.

New hyperfine structure data have been obtained in aluminum in quantum beat spectroscopy measurements using pulsed laser excitation. Hyperfine structure and isotope-shift data have been obtained in barium in two-step excitation in a collimated atomic beam using continuous-wave lasers. The barium results are briefly discussed in terms of hyperfine-induced singlet-triplet mixing.

LIST OF PAPERS

The thesis is based on the following papers:

- I "Hyperfine structure and isotope shift of highly excited barium-I states", P. Grafström, Jiang Zhan-Kui, G. Jönsson, S. Kröll, C. Levinson, H. Lundberg and S. Svanberg, Z. Phys. **A306** (1982) 281.
- II "Intermodulated optogalvanic spectroscopy - a comparison with other high resolution techniques", Ch. Belfrage, P. Grafström, S. Kröll and S. Svanberg, J. Phys. **44** (1983) C7-169 (Colloque C7).
- III "Hyperfine structure and radiative lifetimes in the $3s^2np\ ^2P_{3/2}$ sequence of ^{27}Al using time-resolved laser spectroscopy", G. Jönsson, S. Kröll, H. Lundberg, and S. Svanberg, Z. Phys. **A316** (1984) 259.
- IV "Natural radiative lifetimes in the $3sns\ ^1S_0$ and $3snd\ ^1D_2$ sequences of magnesium", G. Jönsson, S. Kröll, A. Persson and S. Svanberg, Phys. Rev. **A30** (1984) 2429.
- V "Time-resolved laser spectroscopy of high-lying states in neutral oxygen", S. Kröll, H. Lundberg, A. Persson and S. Svanberg, Phys. Rev. Lett. **55** (1985) 284.
- VI "Hyperfine structure measurements in ^{51}V using Doppler-free saturated absorption and polarization spectroscopy", S. Kröll and A. Persson, Opt. Comm. **54** (1985) 277.

ERRATA

The units used in sections IIA, IIB and IIG are inconsistent. To convert the equations in these sections to Gaussian units the factors

$$\frac{h^2}{8\pi^2m}, \quad \frac{1}{4\pi\epsilon_0}, \quad \frac{\mu_0}{4\pi}$$

need to be exchanged against $1/2m$, 1, 1 respectively, whenever they appear.

PAGE

- 16 The summation in the definition of the quadrupole moment is performed over all protons in the nucleus.
- 37 Section A, third line from below, "parallel to the beam", is changed to, "parallel to the laser beam".
- 40 Line 2, "only for a", is changed to, "only for atoms within a".
- 42 The third equation, " $\alpha(l) = \alpha_0/(1+|l|_S)^{-1/2}$ ", is changed to, " $\alpha(l) = \alpha_0/(1+|l|_S)^{1/2}$ ".
- 44 Line 2, "90- θ ", is changed to, " $\pi/2-\theta$ ".
- 46 Subsection 7, ω_m is the modulation frequency of the phase modulator.
- 46 Third line from below, the expression "the techniques above" refers to the saturation spectroscopy techniques described in section C in general.
- 47 The exponent in the equation, " $(-\omega_i t)$ ", is changed to, " $[-(i\omega_i + \Gamma/2)t]$ ", where $1/\Gamma$ is the lifetime of the upper states $|u_i\rangle$.
- 48 Line 6, " $I(t) \sim \sum \sum \langle f_i | \epsilon \cdot \mathbf{D} | u_i' \rangle \langle u_i | \epsilon \cdot \mathbf{D} | f \rangle \exp(-\omega_{ii'} t)$ " is changed to, " $I(t) \sim \sum \sum \langle f | \epsilon \cdot \mathbf{D} | u_i' \rangle \langle u_i | \epsilon \cdot \mathbf{D} | f \rangle \exp[-(i\omega_{ii'} + \Gamma)t]$ ".
- 51 Line 8, " $\sigma_{ik} =$ ", is changed to, " $\sigma_{ik}^{(B)} =$ ".
- 56 Fig. 15, figure text, first line, " $3d^4 4s^2 D_{3/2} -$ ", is changed to, " $3d^9 4s^2 {}^2D_{3/2} -$ ".
- 59 Lines 5-6, "the time associated with changing the velocity of the atoms can be increased by", is changed to, "this ratio can be changed by".
- 66 Three lines above Eq. 23, " $(k = 3 \times 10^{-19} \text{ molecules}^{-1} \text{ cm}^{-1})$ ", is changed to, " $(k = 3 \times 10^{-19} \text{ molecules}^{-1} \text{ cm}^2)$ ".
- 66 Four lines below Eq. 23. The reference given is incorrect. The correct reference is "W.M. USELMAN and E.K.C. LEE, J. Chem. Phys. **65** (1976) 1948.
- 68 The last sentence starting "Eq 24 above . . ." is substituted with "V in Eq. 24 denotes the volume of the part of the laser beam imaged on the photomultiplier tube."

ACKNOWLEDGMENTS

I am deeply indebted to my co-authors Anders Persson, Peter Grafström, Hans Lundberg, Sune Svanberg, Göran Jönsson, Christina Belfrage, Claes Levinson and Jiang Zhan-Kui for everything they have taught me, for all their help in the hard work and all the memorable moments they have given me. This work would not have been possible without their help.

It has truly been a pleasure to have Sune Svanberg as my supervisor. Always being willing to help and with never-ending enthusiasm, he has been an immense support during the years. He has my deepest admiration in all respects.

Numerous discussions with other members of the group have been of great benefit for the work described in the papers as well as in the writing of this thesis. I would especially like to thank Claes-Göran Wahlström, Willy Persson and Håkan Bergström. The technical staff have, with their excellent skill, never failed to solve my problems. I am particularly grateful to Åke Bergquist, who unselfishly always gives a helping hand. My warm thanks to Helen Sheppard for turning the English in this thesis into a more proper form. I also wish to express my gratitude to everyone in the department for the pleasant atmosphere, not forgetting all the initiated discussions and enlightening conversations during lunch.

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I INTRODUCTION

The invention [Maiman 1960, Maiman et al. 1961, Schawlow and Townes 1958] and development [e.g. Javan et al. 1961, Sorokin and Lankard 1966, Schäfer et al. 1966] of lasers [Svelto 1976, Sargent et al. 1974, "Laser Handbook" 1972-] and laser techniques [Demtröder 1982, "High-resolution..." 1976, Svanberg in preparation] have made it possible to manipulate atoms in such a way that their properties are being revealed at a rate and to an extent that were unforeseeable twenty-five years ago. In this thesis laser techniques have been used to add one more piece of information to the vast amount of existing atomic data. In addition developments and studies of laser spectroscopic techniques have been performed.

The introductory chapter consists of two parts. The first part is intended to put the work presented in this thesis into a wider perspective while the second part is an outline of the rest of the thesis.

A Two questions, two answers and a perspective

Two questions relevant to the presentation of any five-year project or working period are:

1. What are the results of the work?
2. How can these results be applied?

1. What are the results of the work?

Firstly, new hyperfine-structure and isotope-shift data (i.e. data on the interactions between the electron cloud surrounding the atomic nucleus and the atomic nucleus itself) have been obtained for three elements (Ba, Al, V).

Secondly, new lifetime data for excited states in three elements (Al, Mg, O) have been obtained (i.e. new data regarding the time the atoms exist in states in which they possess excess energy).

Thirdly, improvements, developments and comparisons have been made for some experimental techniques used for obtaining data of the type described above.

2. How can these results be applied?

The primary users of new data of the type obtained in the papers are theoreticians working in atomic spectroscopy. In order to improve their models of the atom, theoreticians compare atomic quantities calculated from their models with atomic data obtained in experimental measurements. However, the data obtained can also be valuable for researchers in other fields. Especially astrophysicists are using lifetime values to determine the abundance of different elements and compounds at certain places in space. From hyperfine- and isotope-shift data atomic line shapes or line profiles can be predicted. The line profiles for transitions observed in e.g. stellar atmospheres are distorted by collisions and Doppler broadening. Knowledge of the unperturbed line shapes consequently makes it possible to obtain information about the pressure and movements in the stellar

atmosphere. Finally, the work on developing and analysing laser spectroscopic techniques is of interest to experimentalists working in laser spectroscopy and related fields since this enables them to improve or extend their own measurement capabilities.

3. Perspective and outlook

The rapidly growing field of laser spectroscopy is nowadays well established as a primary technique for increasing our knowledge of the atom and its interactions. New exciting directions and applications within this field are arising continuously e.g. laser cooling and trapping [*"Laser Spectroscopy VII"* 1985], ionization in intense laser fields [L'Huillier et al. 1982, Luk et al. 1983, Lambropoulos 1985], inhibited spontaneous emission [Hulet et al. 1985] and other properties of Rydberg atoms in cavities [e.g. Haroche and Raimond 1985, Gallas et al. 1985], the generation of coherent radiation in the VUV and XUV wavelength regions [*"Laser Techniques..."* 1984, Jamroz and Stoicheff 1983] and Rydberg atoms in external fields [Rinneberg et al. 1985, Kleppner et al. 1983, Gay 1984, Clark et al. 1984].

As previously mentioned, a vast amount of atomic data from laser spectroscopic as well as other spectroscopic investigations exists. Consequently the new data presented in this thesis can only fill very small holes in our picture of the atom.

Relating the work done to the users mentioned above, data for all measured states are of potential interest to the theoreticians, while, essentially only the low excited states can be of value for astrophysicists, plasma physicists and other users. Experimentalists in our own field clearly benefit from technique developments in the same way we do. However, there is another group which also has an interest in technique improvements, namely experimentalists working in other areas of research who are already using laser spectroscopic techniques or who may be able to use new laser techniques. Any type of interdisciplinary cross-talk is always very valuable, particularly today when the fields of science are becoming increasingly narrower and the scientists more and more specialized. The route straight ahead is generally the easiest one to follow. Consequently, it is at the borderlines between fields that new ideas and new ways of thinking have the greatest possibility to emerge.

A considerable amount of the work presented in this thesis and in the papers is oriented towards improving and developing experimental techniques. Clearly new techniques need to be developed. This increases the number of applications of the field and makes it move in new directions. However, it is not until these techniques are actually used for obtaining new data that they become really valuable.

To conclude, the work described in this thesis can mainly be seen as one of mankind's innumerable steps towards increasing his knowledge of the world around him following the purely academic tradition. In the present case, knowledge concerning atoms, some of their interactions and of laser spectroscopic techniques has been increased.

B Disposition of the thesis

The aim of this thesis is to recapitulate and discuss the papers with the intention of presenting the work which has been performed in a comprehensive and unified form. A major part of the thesis contains information relevant to this discussion. It contains a fair amount of information for a reader who is interested in details in the papers. However, it mainly concentrates on the physics and contains very few comments about experimental details.

Chapter II gives some aspects on areas of atomic theory related to the work in the papers. References are given to pertinent literature for anyone who is interested in the details or who wishes to pursue the subject more thoroughly. Chapter III discusses some methods which have been used to prepare the atoms to be investigated such that the results of the measurements are unperturbed by external factors. In chapter IV some Doppler-free laser spectroscopy techniques are described. These are mainly of the saturation-spectroscopy-type. Various sources of error in the measurements, some of which have been eliminated or compensated for and some which have not, are described in chapter V. Chapter VI recapitulates the papers and some points or procedures in the papers which may be of particular interest are discussed. Finally, some conclusions are given in chapter VII.

II THEORY

This chapter discusses some details of the atomic structure and interactions which are related to the work presented in the papers.

Section A presents the main type of interactions in the atom. Sections B and C deal with the hyperfine structure and isotope shifts, respectively. These atomic quantities have been measured in papers I, III and VI. Section D contains some comments on the atom-radiation interaction. Natural radiative lifetimes have been measured in papers III, IV and V and photon excitation has been utilized in all experiments. By measuring the atomic properties mentioned above it is possible to, among other things, obtain information about the configuration interaction in the investigated states. Section E mentions some aspects of the configuration interaction and section F deals with Rydberg states. These highly excited states have been studied in papers I, III, IV and to some extent in V. Finally, section G gives some aspects of theoretical and semi-theoretical computational methods. These are Hartree-Fock, multi-channel quantum defect theory and a parametrization based on Sandars and Beck's effective operator formalism.

The present chapter does not cover any of the subjects above in detail. There are various books and review articles that treat the subjects in this chapter more thoroughly. The general structure and main interactions in the atom are described in numerous books at various levels [e.g. Cowan 1981, Lindgren and Morrison 1982, Weissbluth 1978]. A classical work on hyperfine interaction is Kopfermann's "Nuclear moments" [Kopfermann 1958]. Section B in this chapter is, however, largely based on the work of Weissbluth [Weissbluth 1978, chap. 18]. A recent book by King [King 1984] gives extensive information on isotope shifts and it also contains an element-by-element review of all available information that has been obtained in isotope-shift measurements. General information on the atom-radiation interaction can be found in most books on atomic spectra or atomic theory [e.g. Weissbluth 1978, Cowan 1981, Merzbacher 1970]. Cowan also discusses the configuration interaction quite thoroughly. There are various review articles covering different aspects of Rydberg atoms. Two rather recent articles by Fabre [Fabre 1982(a), Fabre 1982(b)] deal with Rydberg states in the alkalis with special emphasis on the radiative properties. A book on Rydberg atoms and molecules has recently been published ["Rydberg states..." 1983]. Rydberg states in the alkaline earths have been the subject of two review articles by Rinneberg [Rinneberg to be published] and Aymar [Aymar 1984]. Aymar's article concentrates on how the interactions in these Rydberg states can be described using multi-channel quantum defect theory (MQDT) and most pertinent references to MQDT can also be found here. Some other recent articles on Rydberg atoms focusing on the interaction between Rydberg atoms and resonant cavities and Rydberg atoms in external fields are [Haroche and Raimond 1985, Gallas et al. 1985, "New trends..." 1984, Feneuille and Jacquinet 1981]. Hartree-Fock theory is thoroughly described by Froese Fischer [Froese Fischer 1977]. The last part of this chapter is denoted "Sandars and Beck's effective operator formalism". It is not focused on the original work by Sandars and Beck [Sandars and Beck 1965], but rather on how the results from this theory

can be used to parametrize hyperfine data as has been done for (primarily) the transition elements by e.g. Childs and co-workers [Childs 1967, Childs et al. 1979]. For a full discussion of how the Sandars and Beck's effective operator formalism is applied to hyperfine structure calculations see e.g. Lindgren and Rosén [Lindgren and Rosén 1974]. Their article also contains a systematic review of experimental hyperfine data obtained for atomic ground configurations up to that date.

A The basic interactions

Atomic physics in general deals with the properties of the electron cloud around the atomic nucleus, and the interactions between the electron and the nucleus, electromagnetic fields, electric fields, magnetic fields or particles. The charge density of the electrons around the nucleus for a specific state denoted by $|a\rangle$ is given by $e|\Psi_a|^2$ where e is the electronic charge and Ψ_a is the solution of the Schrödinger equation

$$H\Psi_a = E_a\Psi_a \quad (1)$$

corresponding to the particular energy E_a . H is the Hamiltonian of the system. The set of solutions to the equation above gives the most complete description that we can obtain for the various states of the atom and from these solutions Ψ_a we can, for each state, calculate the atomic properties we are interested in.

In the absence of external fields the major terms in the (nonrelativistic) Hamiltonian H in Eq. 1 above can be written as

$$H = \frac{\hbar^2}{8\pi^2 m} \sum_{i=1}^N \mathbf{p}_i^2 - \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \frac{Ze^2}{r_i} + \frac{1}{4\pi\epsilon_0} \sum_{i>j}^N \frac{e^2}{r_{ij}} + \sum_{i=1}^N \zeta(r_i) \mathbf{l}_i \cdot \mathbf{s}_i \quad (2)$$

The summations are performed over all N electrons in the atom. The first term represents the kinetic energy of the electrons. $\mathbf{p}_i$ denotes the momentum of electron i . The term $1/r_i$ describes the Coulomb interaction between the nucleus and electron i and the $1/r_{ij}$ term describes the mutual Coulomb repulsion between electrons i and j . The fourth and last term, called the spin-orbit interaction, describes the interaction between the magnetic moment of the electron due to its orbital motion and its spin magnetic moment. Although it is a relativistic effect it is often included in the nonrelativistic Hamiltonian since it may very well (e.g. for multiply charged ions) have a greater influence on the energy than the Coulomb repulsion between the electrons. $\mathbf{l}_i$ and $\mathbf{s}_i$ denote the time average of the orbital and spin angular momentum of electron i , respectively, and $\zeta(r_i)$ gives the strength of the spin-orbit interaction and depends on r_i – the distance between electron i and the atomic nucleus. External fields can be taken into account by substituting $\mathbf{p}$ with

$$(\mathbf{p} - e\mathbf{A}/c)$$

(3)

where $\mathbf{A}$ is the vector potential of the interacting field, and adding a term $e\phi$ where ϕ is the scalar potential for the field. In addition there are some minor relativistic corrections. Together, the terms discussed above describe most properties of an atom with no nuclear spin. However, for an atom with non-zero nuclear spin higher nuclear electric and magnetic moments will interact with the electron cloud and additional corrections need to be included in the Hamiltonian as discussed in the next section.

B. Hyperfine interaction

In addition to the strong Coulomb attraction between the nucleus and the electrons there are other more subtle features in the electron-nucleus interplay. In Eq. 2, the nucleus acts as an electric monopole but it also has higher magnetic and electric moments of which the two with the most pronounced effects are the magnetic dipole moment μ and the electric quadrupole moment $\mathbf{Q}$. The interaction between these moments and the electrons will be briefly described.

1. The magnetic dipole interaction

A vector potential

$$\mathbf{A} = \mu \times \mathbf{r}/r^3$$

is associated with the nuclear magnetic dipole moment. If the momentum $\mathbf{p}$ in the Hamiltonian Eq. 2 is substituted according to Eq. 3 one can show (e.g. [Weissbluth 1978]) that the hyperfine contribution H_{hfs} to the Hamiltonian for a single-electron system will be

$$H_{\text{hfs}} = 2g_I \beta^2 \frac{\mu_0}{4\pi} \left[\frac{\mathbf{l} \cdot (\mathbf{L} - \mathbf{s})}{r^3} + \frac{3(\mathbf{l} \cdot \mathbf{r})(\mathbf{s} \cdot \mathbf{r})}{r^5} + \frac{8\pi}{3} \delta(\mathbf{r}) \mathbf{l} \cdot \mathbf{s} \right] \quad (4)$$

$\beta = eh/4\pi m$ = the Bohr magneton. Consider a charge $-e$ with mass m moving in a circular orbit with angular momentum $h/2\pi$. The magnetic moment in the centre of the orbit calculated using classical electromagnetic theory would then be one Bohr magneton.

μ_0 = the permeability of free space

g_I = the nuclear g-factor, a numerical factor which essentially

describes to what extent the various magnetic moments in the nucleus align. g_I relates the nuclear spin to the nuclear magnetic moment through the relation $\mu = g_I \beta \mathbf{l}$

$\mathbf{I}$ = the nuclear spin

r = the distance between the electron and the nucleus

$\delta(\mathbf{r})$ = the Dirac delta function

With a spin quantum number of 1/2, Eq. 4 can, after integration over the radial part of the wave function, be expressed as

$$H_{\text{hfs}} = 2g_I \beta \frac{\mu_0}{4\pi} \left[\frac{\ell(\ell+1)}{j(j+1)} \left\langle \frac{1}{r^3} \right\rangle \mathbf{I} \cdot \mathbf{J} + \frac{8\pi}{3} |\Psi(0)|^2 \mathbf{I} \cdot \mathbf{s} \right] \quad (5)$$

ℓ and j are the quantum numbers for the orbital angular momentum $\mathbf{L}$ and the total angular momentum $\mathbf{J}$ (excluding nuclear spin).

$$\mathbf{J} = \mathbf{L} + \mathbf{s}$$

$\langle 1/r^3 \rangle$ = the expectation value of $1/r^3$ for the particular state
 $|\Psi(0)|^2$ = the probability that the electron for this particular state is at the nucleus.

The first term is obviously zero for $\ell = 0$ and the second one is zero for $\ell \neq 0$ since (at least in the nonrelativistic limit) only s-electrons have a finite probability of being at the nucleus. Eq. 5 can be written as

$$H_{\text{hfs}} = 2g_I \beta \frac{\mu_0}{4\pi} \left[\frac{\ell(\ell+1)}{j(j+1)} \left\langle \frac{1}{r^3} \right\rangle + \frac{8\pi}{3} |\Psi(0)|^2 \right] \mathbf{I} \cdot \mathbf{J} \equiv A \mathbf{I} \cdot \mathbf{J} \quad (6)$$

Denoting the total angular momentum including nuclear spin by $\mathbf{F}$

$$\mathbf{F} = \mathbf{I} + \mathbf{J} \quad (7)$$

we get

$$H_{\text{hfs}} = (A/2) [F(F+1) - J(J+1) - I(I+1)] \quad (8)$$

A is a constant that is specific for each atomic state. The equation above gives the energy that has to be added to the energy obtained from Eq. 2 to account for the interaction between the nuclear magnetic dipole moment, the electron spin magnetic moment and the orbital angular momentum of the electron. From the general rules for addition of atomic angular momenta we see from Eq. 7 that each level with a specific J splits into $2I + 1$ (assuming $I \leq J$) levels whose energy difference can be calculated from Eq. 8. Thus, from the measured splittings a value for A in Eq. 6 can be deduced and from this we can obtain values for $\langle 1/r^3 \rangle$ and/or $|\Psi(0)|^2$ which can be compared with values obtained from theoretical calculations.

For a multi-electron case Eq. 4 can be written as

$$H_{\text{hfs}} = 2g_I \beta \frac{\mu_0}{4\pi} \sum_{i=1}^N \left[\ell_i \frac{1}{r^3} - \frac{\mathbf{s}_i}{r^3} + \frac{3(\mathbf{s}_i \cdot \mathbf{r})}{r^5} \mathbf{r} + \frac{8\pi}{3} \delta(\mathbf{r}) \mathbf{s}_i \right] \cdot \mathbf{I}$$

where the summation to a first approximation can be chosen to be taken only over the electrons outside closed shells. However, in most cases the interactions are

more complicated and it may no longer be possible to describe the state of interest as a single configuration. Instead, it may be necessary to choose a representation

$$|\Psi\rangle = \sum a_i |\Psi_i\rangle$$

where the sum is taken over all configurations contributing to the actual state and Ψ_i represents the wave function for configuration i and a_i equals $\langle \Psi_i | \Psi \rangle$. One efficient method of describing and parametrize the hyperfine structure for cases where there are many interacting configurations is described in section G in this chapter. However, even in the case of configuration interaction the convenient parametrization in Eq. 8 can be used for the hyperfine structure as long as the total angular momentum J , for the electrons, remains a good quantum number.

The last term in Eqs. 4 and 5 is the so-called Fermi contact interaction. The spin magnetic moment from the electrons at the nucleus interacts with the nuclear magnetic moment and contributes to the total energy of the atomic state. Even if, as stated on the previous page, only s -electrons have a non-zero charge density at the nucleus, non- s -electrons may induce a Fermi contact interaction. Electrons in an outer shell with unpaired spins will affect two paired s -electrons differently. The s -electron with opposite spin will be more strongly repelled by the outer electron. Thus, the spin densities from the the two inner s -electrons will no longer balance at $\mathbf{r} = 0$ and a net Fermi contact interaction results [see e.g. Lindgren and Morrison 1982]. This effect is called spin polarization.

2. The electric quadrupole interaction

The energy (W) in the electrostatic interaction between an electron and the nucleus can be written as

$$W = - \frac{1}{4\pi\epsilon_0} \sum_{p=1}^Z \frac{e^2}{|\mathbf{r}_e - \mathbf{r}_p|} \quad (9)$$

Z is the nuclear charge and $\mathbf{r}_e$ and $\mathbf{r}_p$ are the position vectors for the electrons and protons, respectively. Using standard mathematical techniques we can express the denominator in Eq. 9 as

$$\frac{1}{|\mathbf{r}_e - \mathbf{r}_p|} = 4\pi \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{1}{2\ell+1} \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} Y_{\ell m}^*(\theta_p, \phi_p) Y_{\ell m}(\theta_e, \phi_e) \quad (10)$$

where $r_{>}$ ($r_{<}$) is the largest (smallest) value of $|\mathbf{r}_e|$, $|\mathbf{r}_p|$. The functions $Y_{\ell m}$ are spherical harmonics and θ_p, ϕ_p and θ_e, ϕ_e are the angular coordinates in a spherical coordinate system for the proton and electron, respectively. Inserting Eq. 10 into Eq. 9 and evaluating for $\ell=0$ gives

$$W = - \frac{e^2}{4\pi\epsilon_0} \sum_{p=1}^Z \frac{1}{r_{>}}$$

For non- s -electrons ($r_e > r_p$) we obtain

$$W = -e^2 Z / 4\pi\epsilon_0 r_e$$

For s-electrons, which have a finite probability of being at the nucleus, a correction term [Weissbluth 1978]

$$(2/3)\pi Ze^2 |\Psi(0)|^2 \langle R^2 \rangle$$

has to be added to the energy above. $\langle R^2 \rangle$ is the mean square charge radius of the nucleus and $e|\Psi(0)|^2$ is the electronic charge density at the nucleus. Since the nuclear states have a well defined parity (neglecting the weak interaction), all terms in Eq. 10 which are odd in ℓ disappear in first order perturbation theory. The lowest order correction to the electric monopole ($\ell=0$) in the expansion is then the electric quadrupole term ($\ell=2$). The nuclear moment associated with this term interacts with the field gradient from the electronic charge distribution at the nucleus. For s-electrons the charge distribution is symmetric and the field gradient will be zero. Consequently we may say that $r_e > r_p$ when studying the electric quadrupole interaction. In first order perturbation theory $\ell = 2$ will give

$$W^{(\ell=2)} = -\frac{e^2}{4\pi\epsilon_0} q Q \frac{(3/2)K(K+1) - 2I(I+1)J(J+1)}{2I(2I-1)2J(2J-1)}$$

$$K = F(F+1) - I(I+1) - J(J+1)$$

Q is the nuclear electric quadrupole moment defined as

$$Q = \langle I, M_I=I | \sum_{p=1}^N (3z_p^2 - r_p^2) | I, M_I=I \rangle$$

$|I, M_I=I\rangle$ represents the nuclear wave function

$$M_I = \mathbf{I} \cdot \hat{\mathbf{e}}_z / (h/2\pi)$$

$\hat{\mathbf{e}}_z$ is a unit vector in the z-direction

q is the electric field gradient from the electrons at the nucleus and it is defined as

$$q = - \langle J, M_J=J | \sum_{i=1}^N \frac{3z_i^2 - r_i^2}{r_i^5} | J, M_J=J \rangle = \frac{1}{e} \langle J, M_J=J | \frac{\partial^2 V}{\partial z^2} (\mathbf{r} = 0) | J, M_J=J \rangle$$

the summation is made over all electrons and V is the potential due to the electrons.

C. Isotope shifts

The previous section in this chapter described the energy level splittings in the atom due to interactions between the nuclear and electronic moments. However, for an atom with several isotopes the energy for a specific state will be different for different isotopes. There are two reasons for this. Firstly, the nuclear mass depends on the number of neutrons, secondly the charge distribution in the nucleus will change with the number of neutrons. Consequently the isotope shift is divided into two different parts denoted the mass shift and the field shift, respectively.

1. The mass shift

The origin of the mass shift can be pictured as follows (see e.g. [King 1984]). In all atomic states the angular momentum has a fixed value. Even if the mass of the atom is changed by adding or removing a neutron the angular momenta of all the states still have to be the same. For the angular momenta to remain unchanged for a new mass, the energy must be changed instead. The mass shift can in turn be separated into two different parts. The normal mass shift (also called the Bohr shift or the reduced mass effect) and the specific mass shift.

a) The normal mass shift

Using a classical picture for calculating the term value for a specific energy level we consider an electron with mass m and a nucleus with mass M moving in an orbit around their common centre of mass. This motion can alternatively be expressed as an electron with a reduced mass $\mu = mM/(M+m)$ moving around an infinitely heavy nucleus. A more elaborate treatment using the Schrödinger equation will give the same result [King 1984]. One can (e.g. using the Bohr model with circular orbits) show that the energy or the term value, T , (i.e. the energy required to remove the studied electron from the atom) has an M -dependence in the form of a proportionality factor $M/(M+m)$. It then follows that

$$T_{\infty} - T_M = mT_{\infty}/(M+m) \quad (11)$$

T_{∞} is the term value for an infinitely heavy nucleus

T_M is the term value for a nucleus with mass M

According to the virial theorem for Coulomb interactions we have

$$\langle K \rangle = - \langle V \rangle / 2$$

where $\langle K \rangle$ and $\langle V \rangle$ are the expectation values for the kinetic and potential energy, respectively.

Thus, Eq. 11 can be rewritten as

$$T_{\infty} - T_M = \sum_i \frac{\langle p_i^2 \rangle}{2(M+m)}$$

where the summation, i , is taken over all electrons in the atom. This would then be a generalization of the normal mass shift to the multi-electron case.

b) The specific mass shift

The energy correction due to the mass shift is essentially the kinetic energy of the nucleus, i.e. $P^2/2M$ where $P = |\mathbf{P}|$ and $\mathbf{P} = \sum \mathbf{p}_i$. $\mathbf{P}$ is the momentum of the nucleus and $\mathbf{p}_i$ is the momentum of electron i . The total correction term can then be written

$$T_{\infty} - T_M = \sum_i \frac{\langle p_i^2 \rangle}{2(M+m)} + \sum_{i \neq j} \frac{\langle \mathbf{p}_i \cdot \mathbf{p}_j \rangle}{M+m} \quad (12)$$

A more rigorous treatment is given in [King 1984]. If the motion of the electrons is uncorrelated the term $\langle \mathbf{p}_i \cdot \mathbf{p}_j \rangle$ will average to zero. However, in practice their movements are correlated and the second term in equation 12 will not be zero. The degree of correlation in the electron motion is specific for each state. Thus the second correction term in Eq. 12 is called the specific mass shift. Comparison with theory can be made by calculating the quantity $\sum \langle \mathbf{p}_i \cdot \mathbf{p}_j \rangle$.

2. The field shift

The number of neutrons in the nucleus affects the charge distribution in the nucleus. This changes the electrostatic interaction between the electron cloud and the nucleus. The energy levels will then be different in two different isotopes. The shift in energy due to this effect is denoted the field shift. If there are two isotopes the charge distribution in the heavier of these is normally somewhat more smoothed out and an electron at the nucleus will then experience this as a slightly weaker charge. If we denote the difference in energy for a specific transition in two different isotopes by δE , one may write

$$\delta E \sim \Delta |\Psi(0)|^2 \delta \langle R^2 \rangle$$

$\Delta |\Psi(0)|^2$ = the change in electron density at the nucleus during the transition
 $\delta \langle R^2 \rangle$ = the difference in the mean square radius of the nuclei.

Looking at e.g. an alkali s-p transition, one may as a first approximation neglect the charge density of the p-electron at the nucleus. Thus $\Delta|\Psi(0)|^2 = |\Psi(0)|^2(\text{s-electron})$. An approximation for the s-electron charge density at the nucleus can be obtained either from an empirical relation between this charge density and the magnetic dipole coupling constant for the particular state [King 1984] or from the Fermi-Goudsmith-Segré formula

$$|\Psi(0)|^2(\text{ns}) = \frac{1}{\pi a_0^3} \frac{ZZ_A^2}{(n^*)^3} \frac{dn^*}{dn}$$

a_0 = the Bohr radius

Z = the nuclear charge

Z_A = the spectrum number (1 for neutral, 2 for singly ionized and so on)

n^* = the effective principal quantum number

n = the principal quantum number

In practice, the condition $\Delta|\Psi(0)|^2 = |\Psi(0)|^2(\text{ns})$ is not correct. A better expression is

$$\Delta|\Psi(0)|^2 = \beta |\Psi(0)|^2(\text{ns}), \quad 0 < \beta < 1$$

where β , the screening factor, accounts for effects like the shielding of the s-electron by other electrons. Screening effects can be measured by comparing a specific electron transition for two different ionization stages in an element. E.g., comparing the $5d^{10}6s^2 - 5d^{10}6s6p$ transition in a neutral element with the $5d^{10}6s - 5d^{10}6p$ transition in the first ionization stage of the same element will give information on to what extent the two s-electrons shield each other. In field shift measurements comparisons with theory can for example be done by *ab initio* calculations of $\Delta|\Psi(0)|^2$ or $|\Psi(0)|^2$ if $\delta\langle R^2 \rangle$ is known from nuclear physics.

After subtraction of the normal mass shift the isotope shift can be written as $IS = FS + SMS$ (FS=field shift, SMS=specific mass shift). As discussed in this section, the FS can be factorized into one transition-dependent and one isotope-dependent contribution. This can be used for separating the FS and the SMS components. One way to do this is to use the so-called King plot [King 1963, King 1984].

D. Interaction between atoms and radiation

The interaction between an atom and a radiation field can be incorporated into the Hamiltonian by introducing the vector potential $\mathbf{A}(\mathbf{r}, t)$ of the radiation field. From Maxwell's equations we have for the magnetic ($\mathbf{B}$) and electric ($\mathbf{E}$) fields

$$\mathbf{B} = \nabla \times \mathbf{A}$$

$$\mathbf{E} = -\nabla\Phi - (1/c)(\partial\mathbf{A}/\partial t)$$

where Φ is the scalar potential for the electric field. As for the vector potential associated with the nucleus in section B.2 we replace the momentum $\mathbf{p}$ of the electron with $(\mathbf{p} - (e/c)\mathbf{A})$. The Hamiltonian for the atom-radiation interaction (H_{int}) then becomes [Weissbluth 1978]

$$H_{\text{int}} = \frac{e}{mc} \mathbf{p} \cdot \mathbf{A} + \frac{e^2}{2mc^2} \mathbf{A}^2 + \frac{eh}{2\pi mc} \mathbf{S} \cdot (\nabla \times \mathbf{A}) \quad (13)$$

The radiation field is a function of photon energy and photon polarization and can be expressed as

$$\mathbf{A}_{\mathbf{k}q} = \sum_{\mathbf{k}q} \hat{\mathbf{e}}_{\mathbf{k}q} A_{\mathbf{k}q} \left[a_{\mathbf{k}q} e^{i\mathbf{k} \cdot \mathbf{r}} + a_{\mathbf{k}q}^\dagger e^{-i\mathbf{k} \cdot \mathbf{r}} \right]$$

$\mathbf{k}$ = the wave vector

$\mathbf{r}$ = the position in space

q = the state of polarization (two orthogonal components)

$\hat{\mathbf{e}}_{\mathbf{k}q}$ = the unit vector in the polarization direction

$A_{\mathbf{k}q}$ = a factor proportional to the amplitude of the electric field

$a_{\mathbf{k}q}$ and $a_{\mathbf{k}q}^\dagger$ = photon annihilation and creation operators

In the equation above we can make the following expansion

$$\exp(i\mathbf{k} \cdot \mathbf{r}) \approx 1 + i\mathbf{k} \cdot \mathbf{r} + \dots$$

Neglecting $i\mathbf{k} \cdot \mathbf{r}$ and higher order terms is equivalent to saying that the radiation field can be treated as a plane wave or at least a summation of plane waves over the size of the atom. This approximation is generally referred to as the electric dipole approximation. In the first order perturbation approach $\langle a | H_{\text{int}} | b \rangle$ will then be proportional to $\langle a | \mathbf{p} \cdot \hat{\mathbf{e}}_{\mathbf{k}q} | b \rangle$ which in turn is proportional to $\hat{\mathbf{e}}_{\mathbf{k}q} \cdot \langle a | \mathbf{r} | b \rangle$. The next higher term in the expansion ($i\mathbf{k} \cdot \mathbf{r}$) will give an antisymmetric term containing $\mathbf{r} \times \mathbf{p}$ and a symmetric term containing an electric quadrupole operator. The term containing $\mathbf{r} \times \mathbf{p}$ is proportional to the orbital magnetic moment $\mu(\ell)$. This term, together with the last term in Eq. 13 containing the spin magnetic moment, contributes to the magnetic dipole transitions. To calculate two-photon processes one can make a second order perturbation expansion of the $\mathbf{p} \cdot \mathbf{A}$ term and include the term proportional to $\mathbf{A}^2$ in Eq. 13. With these terms one can describe two-photon absorption and emission and elastic and inelastic scattering processes.

The aspect of the atom-radiation interplay studied in this thesis is the spontaneous decay of excited atomic states by emission of a photon. The process follows an exponential decay and the probability of observing the decay from a specific state $|e\rangle$ as a function of time (t) can be written

$$P(t) \sim \exp(-t/\tau_e)$$

where τ_e is called the natural radiative lifetime for the state $|e\rangle$.

Finally, this section will define some quantities related to the natural lifetime of a state. The transition probability per unit time (A_{ef}) for a spontaneous transition $|e\rangle \rightarrow |f\rangle$ is related to τ_e by

$$\tau_e = (\sum A_{ef})^{-1}$$

where the summation is performed over all lower states $|f\rangle$ in the atom. A_{ef} can be expressed as

$$A_{ef} \sim \omega_{ef}^3 \sum_{f_e} \sum_{f_e} |\langle f | \sum_i \mathbf{r}_i | e \rangle|^2$$

where the summation $\sum_i \mathbf{r}_i$ is made over all electrons i in the atom and the other summation is made over all degenerate levels within $|f\rangle$ and $|e\rangle$. If a radiation field is present, stimulated emission as well as absorption of photons may occur. The total emission rate (W_{tot}) per atom and unit time can then be written

$$W_{tot} = A_{ef} + B_{ef}\rho(\nu)$$

B_{ef} is the Einstein coefficient for stimulated emission.

$\rho(\nu)$ is the spectral energy density, i.e. the energy of the radiation field per unit volume and unit frequency. E.g. the intensity, I , (units W/m^2) for a plane propagating wave is related to $\rho(\nu)$ by

$$I = c \int \rho(\nu) d\nu$$

c is the speed of light

B_{ef} is related to A_{ef} (the Einstein coefficient for spontaneous emission) by

$$B_{ef} = \frac{2\pi^3 c^3}{h\omega_{ef}^3} A_{ef}$$

ω_{ef} is the transition frequency for the transition $|e\rangle \rightarrow |f\rangle$.

E. Configuration interaction

Consider an N -electron atom. The N electrons occupy N different spin orbitals. In the mathematical description of the atom each orbital is specified by a unique set of quantum numbers. These define the spin and orbital angular momentum of the electron as well as the average distance from the nucleus. To a first approximation a multi-electron wave function is constructed by an antisymmetric product of these N orbitals (antisymmetric with respect to interchanging two electrons). This multi-

electron wave function is called a Slater determinant. However, in the real atom it may not be possible to describe the electron wave function by a single Slater determinant. But since the mathematical description that is used for the atomic orbitals constitutes a complete set, any atomic state can always be expressed as a linear combination of Slater determinants. Since, in the general case, an infinite number of Slater determinants may be needed to characterize a state exactly, calculating atomic observables for such a state can be difficult. Thus, it is important to characterize a state as well as possible with a limited number of Slater determinants. For a specific state the largest contributions generally come from configurations with the same spin, angular and total angular momentum which are also close-lying in energy. One (perhaps naive) way of picturing the configuration interaction (CI) is to say that these orbitals are so similar that the electrons do not know which of these orbitals they occupy. Over the years a substantial effort has been put into elucidating the mechanisms and processes which govern the CI. The interplay between different configurations can also be clearly seen in some of the papers in this thesis.

It is often possible to select a rather limited set of basis states (as basis states e.g. pure LS or jj coupled wave functions could be used) as the main contributors to a real state. Firstly, only states $|b\rangle$ where $\langle b|H|a\rangle \neq 0$ will interact with a state $|a\rangle$, (H is the Hamiltonian). Since H has even parity, only configurations $|b\rangle$ which have the same parity as $|a\rangle$ will contribute. H contains one- and two-electron operators. Thus two interacting configurations may, at the most, differ by two electrons. Furthermore, if we have a clean-cut coupling situation for the angular momentum this will also limit the number of contributing states. E.g. LS coupling: L , S and J are good quantum numbers. Thus we must have $L_a = L_b$, $S_a = S_b$, $J_a = J_b$ for an interaction between $|a\rangle$ and $|b\rangle$. CI is often strong when the configurations have the same parity and the same set of principal quantum numbers. Configurations with these properties are said to belong to the same complex. Three configurations which belong to the same complex are e.g. $3s4p^2/3s4d^2/3p4s4p$, where the quantum numbers refer to electrons outside the first and second closed shells. The CI will be especially strong in the case above if the energies for these configurations are roughly the same. This is generally the case for highly ionized states where the energy is mainly determined by the principal quantum number and only to a minor extent by the azimuthal quantum number (l). Finally a few other cases where the configuration interaction can be expected to be strong will be mentioned. One such case is between configurations $nsnp^{A+1}/ns^2np^{A-1}n'd$ for all n' in neutral atoms. The CI in this case is particularly strong for $n=3$ [Cowan 1981]. The configurations $(n+1)snd^{A+1}/(n+1)s^2nd^A/nd^{A+2}$ often interact strongly in the transition elements and in Rydberg series interactions between configurations $nl^An'l' / nl^An''l'$ can sometimes be of substantial importance [Persson and Wahlström 1984].

F. Rydberg atoms

The Rydberg states are excited states for which one electron has a considerably larger principal quantum number than the other electrons. When the outer electron is far out from the other electrons and the nucleus their influence on the outer electron can, to a good approximation, be described as that of a point charge at the nucleus. Thus these states behave rather like hydrogen. This is very fortunate because the Schrödinger equation for hydrogen can (in the absence of external magnetic fields) be solved exactly. It also turns out that several of the observable properties scale in a very regular way as a function of principal quantum number (n). Some examples are given in TABLE I.

TABLE I	
This table shows how some atomic properties scale in a hydrogen-like atom as a function of the principal quantum number (n).	
quantity	scale as n raised to power
average radius of orbit	2
natural radiative lifetime	3
hyperfine structure	-3 *
binding energy for the eletron	-2
energy splitting between neighbouring states in a Rydberg series	-3
critical field strength for field ionization	-4

*This is however true only if the hyperfine structure arises from an interaction between the outer electron and the nucleus, and not if the hyperfine structure arises, for example, from the Fermi contact interaction between a low-lying unpaired s-electron (unpaired means here that in an $\ell=0$ sub-shell there is only one electron present). This hyperfine structure will then not be sensitive to the radius of the orbit of an outer electron.

The scaling laws in TABLE I are applicable to Rydberg states in any atom provided that the principal quantum number n is changed to an effective principal quantum number n^* . Generally we have $n^* < n$. We can picture this apparent reduction in principal quantum number as a tendency for the outer electron to spend some time inside the electron cloud formed by the other electrons. It then sees a nuclear charge which is higher than one atomic unit charge (we now refer to neutral atoms) and will then be more tightly bound. This effect will be especially strong

for s-electrons.

However, deviations from these scaling laws occur. There can be doubly excited states with the same parity and total angular momentum as the Rydberg states. Configuration interaction may then cause the measured values to be quite different from what would be expected from the simple scaling laws. Thus, this configuration interaction can be probed experimentally. Lifetimes of Rydberg states are particularly sensitive for probing interactions with doubly excited states [Aymar *et al.* 1982, Bhatia *et al.* 1981]. This can also be seen for lower states as is the case in paper IV on magnesium. In Berlin extensive studies have been done on hyperfine structure in Rydberg states by Matthias, Rinneberg, Beigang and co-workers. They have demonstrated that the hyperfine structure induced by the Fermi contact interaction by an unpaired low-lying s-electron is extremely sensitive to singlet-triplet mixing [Matthias *et al.* 1983, Rinneberg and Neukammer 1982(a), Beigang *et al.* 1981]. The singlet-triplet mixing may in turn have been induced by the Fermi contact interaction itself or by the presence of doubly excited states. This effect can also be observed in the results presented in paper I on barium. Rydberg states are also interesting because of the possibility of studying interactions between atoms and electric or magnetic fields under conditions where the influence of these on the outer electron is comparable to the influence from the Coulomb interaction between this electron and the core.

G. Methods of computation

Even if all the papers in this thesis are based on experimental measurements, it may be of interest to briefly sketch some commonly used theoretical computation schemes and methods for calculating atomic observables. A firm connection between theory and experiment is one of the prime conditions for successful research. This does not necessarily mean that the same persons have to handle both theory and experiment, but both groups profit from being aware of each others' possibilities and limitations. The following methods for computation or analysis will be mentioned: Hartree-Fock, Multi-channel Quantum Defect Theory (MQDT) and Sandars and Beck's effective operator formalism.

1. Hartree-Fock theory

The Hartree-Fock theory is one of the main techniques for *ab initio* calculations of atomic properties. Let us, however, begin by looking at the Schrödinger equation again and limit ourselves to the three usually most important terms.

$$\left[\frac{\hbar^2}{8\pi^2 m} \sum_{i=1}^N \nabla_i^2 - \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \frac{Ze^2}{r_i} + \frac{1}{4\pi\epsilon_0} \sum_{i>j}^N \frac{e^2}{r_{ij}} \right] \Psi = E\Psi \quad (14)$$

E is the energy of a specific state and Ψ is a Slater determinant. The second term is spherically symmetric and depends only on the distance between the nucleus and the electron. Solving the equation would be considerably easier if the third term were also spherically symmetric. Thus as an approximation we may choose an

approximate Hamiltonian (H')

$$H' = \frac{h^2}{8\pi^2 m} \sum_{i=1}^N p_i^2 - \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \frac{Ze^2}{r_i} + \frac{1}{4\pi\epsilon_0} \left\langle \sum_{i>j}^N \frac{e^2}{r_{ij}} \right\rangle$$

where $\langle \rangle$ represents the spherically symmetric part. The solution to $H'\Psi = E'\Psi$ can be chosen as a product of single-electron wave functions antisymmetrized with respect to interchanging two of the electrons. The single-electron functions are of the type

$$\Psi_{n\ell m m_s}(\mathbf{r}, m_s) = (1/r) P_{n\ell}(r) Y_{\ell m}(\theta, \phi) \xi(m_s)$$

n = the principal quantum number

ℓ = the orbital quantum number

m = the projection of ℓ along the z -axis

m_s = the projection of the electron spin along the z -axis

$P_{n\ell}$ = the radial wave function

$Y_{\ell m}$ = the spherical harmonics

$\xi(m_s)$ = the electron spin function

In this equation we do not know the radial wave function $P_{n\ell}$ until the potential has been specified further. It may be worth mentioning that the noncentral part of the third term in equation 14 causes the splitting of configurations into terms according to the orbital and spin angular momentum of the solutions. (The spin-orbit interaction then splits the terms in fine structure levels according to the total angular momentum of the state.)

In the Hartree-Fock approach Eq. 14 for the Slater determinant is reduced to a set of N coupled integro-differential equations, one for each electron, of the type

$$H_i \Psi_i = E_i \Psi_i \quad (15)$$

The Hamiltonian in this case consists of four terms: the kinetic energy of the electron, the potential energy for the electron in the field from the nucleus and two terms describing the Coulomb interaction with the other electrons. For one orbital, i , these last two terms can be written as

$$\frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \left[\int \Psi_j^*(\mathbf{r}) \frac{e^2}{|\mathbf{r}_i - \mathbf{r}|} \Psi_j(\mathbf{r}) d^3\mathbf{r} \right]$$

where the summation over j is made over all other electrons in the atom and

$$- \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \left[\int \Psi_j^*(\mathbf{r}) \frac{e^2}{|\mathbf{r}_i - \mathbf{r}|} \Psi_i(\mathbf{r}) d^3\mathbf{r} \right] \delta(m_s^i, m_s^j)$$

This last term (called the exchange term) is zero if Ψ_i and Ψ_j have opposite spin. The exchange term, which results from the antisymmetrization of the wave function

causes the electrostatic interaction to be stronger between electrons of opposite spin than between electrons with the same spin.

There is no general analytical solution to the set of coupled equations above. Especially, solving the equation for one of the orbitals requires a complete knowledge of all the other orbitals as can be seen from the terms above. Some kind of self-consistent iterative procedure then seems to be appropriate. For calculating the third and fourth terms in Eq. 15, orbitals calculated in the central field approximation turn out to be a good starting point. To assume that the central field spin orbitals can be used is a convenient approach since the angular part of the wave function can then be separated from the radial part and solved once and for all. To simplify the calculations further one can assume that the radial wave functions are only dependent on the quantum numbers n and l and not on m and m_s (i.e. electrons in the open shells are assumed not to affect the inner electrons by spin or orbital polarization). This will reduce the number of coupled equations in r from being the same as the number of electrons (N) to being equal to the number of occupied electron shells (M). This approach is called restricted Hartree-Fock. The wave functions obtained with the restricted Hartree-Fock approach provide a good starting point for more accurate calculations such as Many-Body Perturbation Theory [Lindgren and Morrison 1982], Multi-Configuration Hartree-Fock [Froese Fischer 1977] or Relativistic Hartree-Fock [e.g. Lindgren and Rosén 1974] where effects like spin polarization, electron correlation, configuration interaction and/or relativistic effects can be taken into account.

Hartree-Fock is a variational method where one tries to minimize the energy of a particular state or core. For calculations concerning states above the ground state one must incorporate the condition that the wave functions must be orthogonal to the wave functions of the lower states. Calculations beyond the restricted Hartree-Fock scheme rapidly increase the time needed for the computation.

2. Multi-Channel Quantum Defect Theory

Multi-Channel Quantum Defect Theory (MQDT) is no ab initio theory, but it gives a very simple parametrization of data in e.g. a Rydberg sequence. The admixture coefficients for interacting configurations are obtained directly from fits to experimental data. Thus MQDT has a very direct connection to experimental work which may be very encouraging for the experimentalist. MQDT offers a method of describing all states within a whole Rydberg series and the continuum above in a very condensed form. From this description atomic observables can be calculated with reasonable accuracy. Briefly, MQDT can be described as follows.

We wish to obtain the wave function for one (or normally several) state(s). As a starting point we choose a case where an electron with known angular momentum is scattered by an ion with known energy and angular momentum. We specify the coupling between the angular momenta (jj -coupling) of the ion and the electron but not the energy of the electron. We can describe this situation with a wave function Ψ_i . This wave function represents a so-called collision channel. We associate a collision channel with each of the Rydberg series we want to include in our

description. For a specific Rydberg series only series which are expected to interact with this are included. As the electron approaches the ion the description outlined above for the interaction at large distances is no longer correct. Exchange effects, electron correlation and other interactions need to be taken into account. In this situation with close range interactions there is another set of wave functions, the so-called, close coupling wave functions which better describes this interaction. Alternatively the collision can also be described by a scattering matrix (S) from which we, with knowledge of the initial collision channel, can obtain the scattering amplitude into the other collision channels for the electron on its path away from the ion. There exists a unitary transformation matrix which diagonalizes S. This matrix is also a transformation between the collision channels and the close coupling channels. The wave function for a specific state Ψ can be written as a sum of wave functions for the close coupling channels Ψ_α , $\Psi = \sum A_\alpha \Psi_\alpha$. The conditions that the wave functions should be continuous when going from the collision coupled to the close coupled channels and that the wave function for bound states should go to zero as r goes to infinity imposes restrictions on the transformation matrix, the eigenvalues of the scattering matrix and on the mixing coefficients (A_α). We can also express the wave function Ψ_n for a specific state $|n\rangle$ as a sum of wave functions for the collision coupled channels $\Psi = \sum Z_{in} \Psi_i$ where the mixing coefficients Z_{in} depend on the elements in the transformation matrix, the eigenvalues of the scattering matrix and the effective principal quantum number of the state $|n\rangle$. The restrictions mentioned earlier will lead to an equation for each state $|n\rangle$. These equations will contain the elements of the transformation matrix, the eigenvalues of the scattering matrix and the effective principal quantum number for the states. The first two sets of parameters are unknown but the effective principal quantum numbers are readily obtained from experimental data. In MQDT one now performs a fit of the first two sets of parameters such that the equations for fulfilling the boundary conditions are satisfied, or as nearly satisfied as possible, for all states. After the fit we know the transformation matrix and the eigenvalues. The mixing coefficients Z_{in} can then be calculated for all states in all Rydberg series which consist of the interacting collision channels we have included in the treatment. For these states, where we now have an analytic form for the wave functions, the properties measured can readily be calculated.

3. Sandars and Beck's effective operator formalism

For configurations with several open shells calculations of the MCHF type easily become quite involved due to the strong configuration interaction. The Sandars and Beck formalism offers a method of converting the measured hyperfine structure into a set of parameters which can either be calculated theoretically or (and) can be used to predict the hyperfine structure in other terms in the configuration. Only the magnetic dipole interaction will be discussed here, however, higher order interactions are treated in a completely analogous fashion.

We can rewrite the hyperfine operator in Eq. 4 (excluding the nuclear spin) as

$$H_{\text{hfs}} = 2g_I \beta^2 \frac{\mu_0}{4\pi} \left[\mathbf{L} \langle r^{-3} \rangle_{01} - \sum_{i=1}^N \sqrt{10} (\mathbf{s}_i C^2) \langle r^{-3} \rangle_{12} + \mathbf{S} \langle r^{-3} \rangle_{10} \right] \quad (16)$$

$$\mathbf{L} = \sum_{i=1}^N \mathbf{l}_i$$

$$\mathbf{S} = \sum_{i=1}^N \mathbf{s}_i$$

$$C^2 = (1-3\mathbf{r}\mathbf{r})/\sqrt{10}$$

$\langle r^{-3} \rangle_{ij} =$ adjustable parameters to be fitted to experimental data

The operator above acts only on the angular part of the wave functions. The $\langle r^{-3} \rangle$ parameters which from left to right are the orbital, spin-dipole and Fermi contact contributions are treated as numbers. The angular factors in front of the $\langle r^{-3} \rangle_{ij}$ parameters are tensors of rank j in orbital space and rank i in spin space. The summation for the spin-dipole part is taken over all electrons in open shells otherwise the notation is the same as in Eq. 4. The angular coefficients above have been evaluated explicitly for the configurations l^N and $l^{N-1}l'$ by Childs [Childs 1967, Childs 1970]. From term analysis we can get the interacting LS configurations that constitute a specific state and for all these LS configurations the coefficients in front of the effective $\langle r^{-3} \rangle_{ij}$ parameters can be calculated. The measured A-factors can be calculated from Eq. 8. From these, values can be assigned to the $\langle r^{-3} \rangle$ parameters such that Eq. 16 represents the measured hyperfine structure as well as possible. The $\langle r^{-3} \rangle$ parameters can then, on the other hand, be calculated theoretically for the specific LS configurations. The deviations between theoretical and experimental values then give information on, for example, relativistic effects or additional configuration interaction not taken into account.

III PRODUCTION OF FREE ATOMS

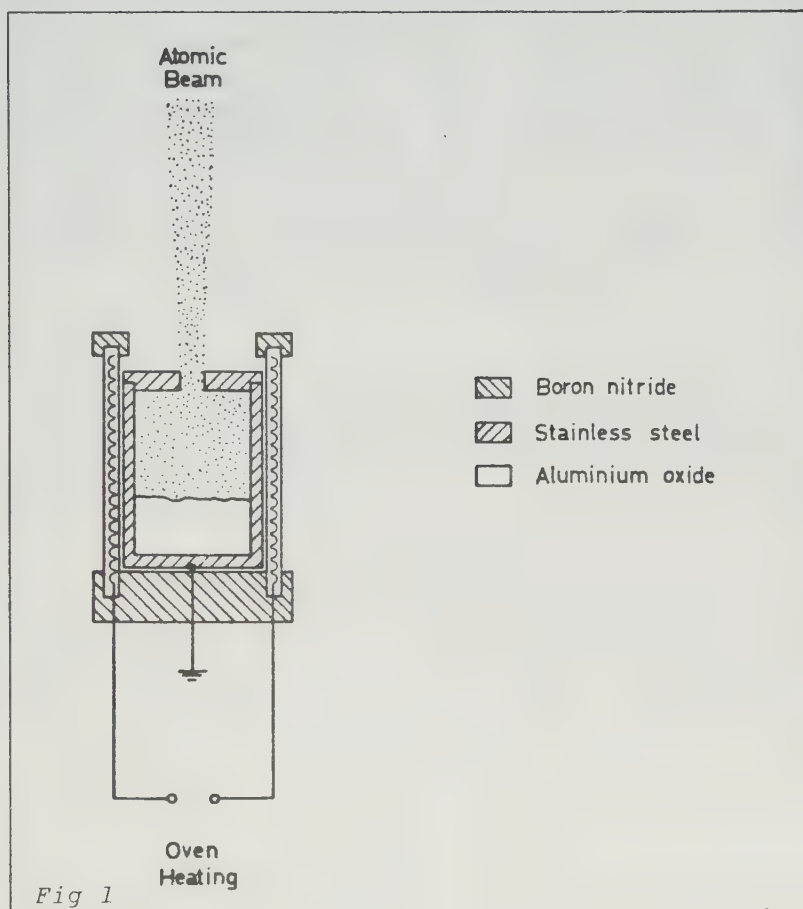
A general problem in measurements of atomic properties is to prepare the atoms to be investigated such that effects of other atoms or external fields do not affect the results. This chapter contains a presentation of the techniques used in the papers in this thesis.

These are:

- 1) Forming an atomic beam by resistive heating of the atomic sample. Evaporated atoms are effused through a small hole in the oven and the beam is formed.
- 2) Sputtering of the cathode material in a hollow cathode discharge. In the discharge metastable and excited states in carrier gas and cathode material atoms are populated.
- 3) Photodissociation of molecular gases where atoms of the element to be investigated are one of the constituents in the molecule.

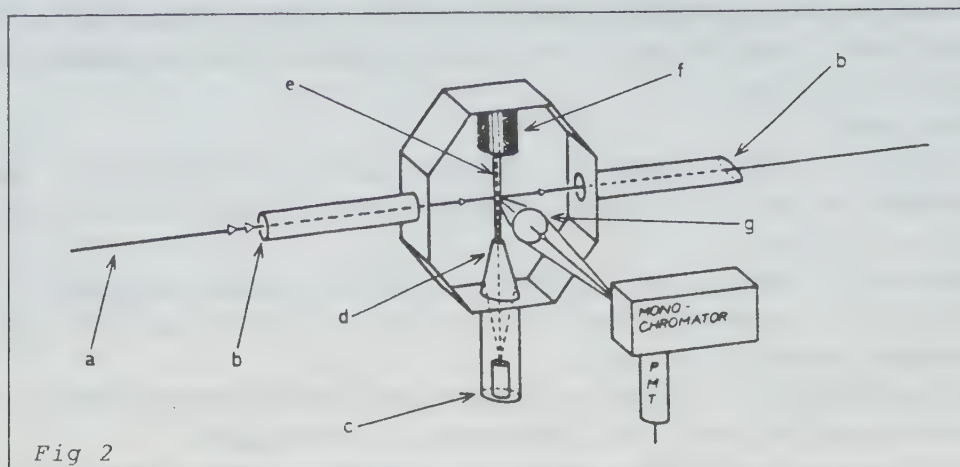
A. Creating a (collimated) atomic beam by resistive heating

An effective technique for producing free atoms of several elements is to put the sample in a resistively heated oven (see Fig. 1).



Schematic drawing of the atomic beam oven. The width of the oven is a few centimetres.

Figure 1 shows one type of oven used in our experiments. The oven is then placed in a vacuum system as shown in Fig. 2.

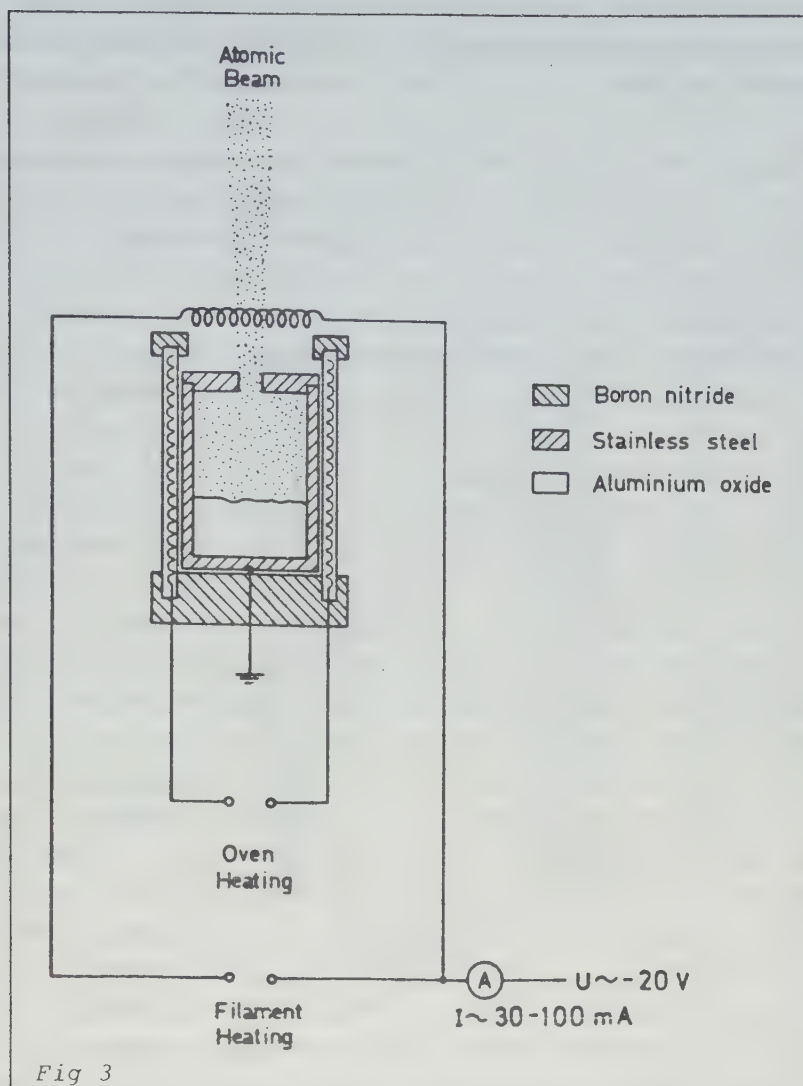


This drawing shows some details of the vacuum system used for the experiments in papers I, III and IV. a) incoming laser beam, b) entrance and exit windows. After entering (and before exiting) the vacuum chamber the laser beam passes through 0.5 m long tubes. The insides of these tubes as well as the main body of the vacuum chamber are painted black in order to minimize stray light. c) oven. This is placed in the lower part of the vacuum chamber. d) aperture for collimating the atomic beam if necessary, e) atomic beam. f) cold-trap. The atoms in the atomic beam will freeze onto this liquid-nitrogen-cooled metal container. The cold-trap helps to keep down the pressure in the system. g) light-collecting optics. Opposite this lens is a 15 cm wide tube leading to the diffusion pump. Thus the photomultiplier looks directly into this black hole.

The oven is heated by passing a current through the heating wire, thereby evaporating the sample. The higher pressure in the oven will force the atoms through the small hole. As they go through the hole into the collision-free high-vacuum region they will move in a straight path. By choosing suitable apertures a well collimated atomic beam can be formed in the interaction region.

A slight reconstruction of the oven makes it possible to populate metastable states [Jönsson et al. 1984(a), Garpman et al. 1971, Brinkmann et al. 1969] and also to create atomic ions [Jönsson et al. 1984(b), Jönsson private communication]. Metastable states may be populated by running a DC discharge at the oven orifice. The reconstructed source is shown in Fig. 3 (taken from Jönsson et al. 1984(a)).

By varying the current through the heating wire and/or the cross section of the wire, temperatures ranging from 300–1500 K can easily be obtained. The technique is useful for elements which have vapour pressures of about 10^{-3} torr (~ 0.1 Pa) at these temperatures. With an appropriate choice of apertures along the beam a collimation ratio of about 100:1 can be achieved. For Doppler-free spectroscopy, as described in paper I in this thesis, it is often mainly the collimation ratio that limits the spectral resolution in the experiment. In lifetime measurements or hyperfine structure measurements using quantum beat spectroscopy, as described in papers III – V, this is not a problem.



A slight reconstruction of the oven depicted in Fig. 1 makes it possible to populate metastable states in the atomic beam (from Jönsson et al. 1984 (a)).

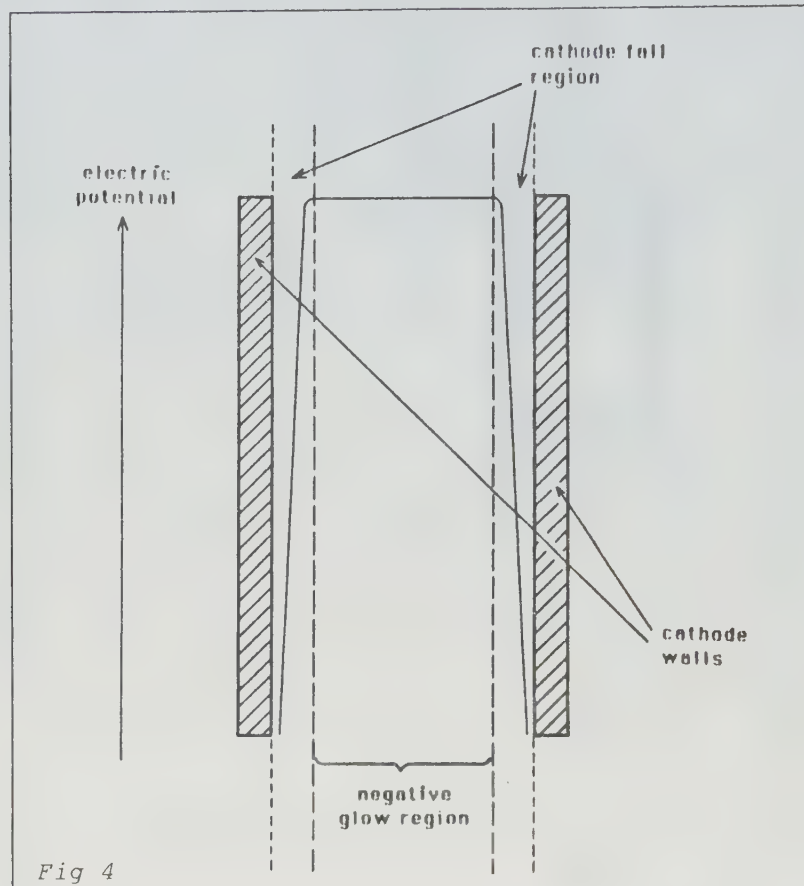
The technique is not applicable to all elements since there is an upper limit on the temperature that can be obtained. Other drawbacks are that the heating wire burns out and has to be changed, especially when running at high temperatures, and one batch of sample material will not last for a whole measurement. This means that the vacuum system must be opened and the oven dismantled and reloaded which delays the data collection until the system has been evacuated again.

B. Sputtering in a hollow cathode discharge

For laser spectroscopic investigations of the type presented in this thesis there are two types of elements for which a hollow cathode (HC) can be particularly advantageous compared with an atomic beam apparatus for producing atoms. Rare gas atoms can be studied since the high-lying metastable states are very efficiently populated in the discharge. Furthermore, atoms of refractory elements can be produced at high densities by sputtering. Metastable as well as ionic states

are then populated in the discharge [de Hoog *et al.* 1977] and can be studied using Doppler-free spectroscopy [Gerstenberger *et al.* 1979].

A sketch of the transverse profile of the electrical potential in a hollow cathode is shown in Fig. 4.



The electric potential across the hollow cathode. The dashed lines are guide lines for the eye showing the extension of the cathode fall region and the negative glow region. The solid line represents the electric potential between the two cathode plates. There is a strong electric field at the cathode walls (the cathode fall region), but at the centre of the hollow cathode (in the negative glow region), where the potential is flat, there is a volume with essentially no electric field.

Two regions can be seen in the figure, one where the potential is almost flat which is called the negative glow region and one at the cathode walls where the potential drops rapidly. This is called the cathode fall region and the voltage drop over the HC is almost exclusively confined to this region.

The discharge is predominantly sustained by electrons created in the cathode fall region oscillating back and forth between opposite cathode walls. The electrons will excite and ionize atoms in the discharge on their way. Some of the ionized carrier gas atoms will reach the cathode fall region and be accelerated in the strong field. Accelerating towards the cathode wall the carrier gas ion hits other carrier gas atoms. The probability of charge transfer in these collisions is quite high. Gaining an electron from a nearby carrier gas atom the former ion is

towards the cathode wall but soon a new charge transfer occurs and so on. Due to the charge transfer processes the kinetic energy of the carrier gas ion finally impinging on the cathode surface is not more than some ten electron volts (eV). Secondary electrons will be emitted at the impact as well as a small number of atoms of the cathode material.

Wehner and co-workers measured the sputtering yield for various carrier gases and cathode materials in the early sixties [Laegreid and Wehner 1961, Rosenberg and Wehner 1962]. The sputtering efficiency for a specific carrier gas as a function of the mass number of the sputtered element can roughly be described by the product of two functions [Warner private communication]; - one smooth function which essentially peaks when the cathode material and carrier gas atoms have the same masses and one function increasing with the number of electrons in the outer unfilled d-shell. This function is more or less constant until the d-shell is about half filled and then rises sharply. Thus the sputtering efficiency is good for Cu, Ag and Au while it is about a factor of four lower for, e.g., V, Nb or Ta. The sputtering efficiency is very low at ion energies of about 10–30 eV [e.g. Pillow 1981]. Essentially, the sputtering efficiency has a threshold at about 25 eV, but it is still very low at 30 eV. Consequently, carrier-gas sputtering will not be very efficient. However, some cathode atoms will still be sputtered and some of these will also become ionized in the plasma. As these cathode material atoms eventually reach the cathode fall region again and are accelerated they will not undergo charge transfer very often, simply because they only encounter very few atoms of their own kind. Impinging on the cathode surface with a considerable energy they will be reasonably efficient in sputtering and this is the main sputtering process in a hollow cathode discharge. These processes are treated both qualitatively and quantitatively by Warner and co-workers [Warner et al. 1979].

It would be interesting to get an estimate of the order of magnitude of various atom (or ion) concentrations in the HC. Interest in developing lasers where the atoms of the active medium are sputtered and the upper laser level is populated in a hollow cathode discharge has caused a substantial amount of data of this type to be produced [van Veldhuizen and de Hoog 1984, de Hoog et al. 1977, Pillow 1981]. The numbers measured depend, of course, on discharge conditions such as pressure, current, carrier gas, cathode material and also on the geometry and size of the HC. However, for a discharge where the cathode consists of two parallel planar plates separated by a distance d , discharge characteristics taken at one distance can be scaled such that it is possible to predict what will be observed in a similar cathode with a different plate distance. These so-called similarity rules [von Engel 1965, Lawler 1981] say that if two planar cathodes which are identical with the exception that their linear dimensions differ by a factor k are run at the same operating current and voltage the cathode with the larger dimensions has a pressure which is a factor $1/k$ lower and a space charge density which is a factor $(1/k)^2$ lower than the smaller one.

It seems reasonable to assume that the metal atom density scales in a similar way. The reason for this is that the sputtering of the metal atoms (as long as the current is not too low) is predominantly achieved by metal ions and the main channel for creating the metal ions is by charge transfer between metal atoms and buffer ions [Warner et al. 1979, van Veldhuizen and de Hoog 1984]. To make some kind of estimate of the densities of some of the discharge constituents it is assumed that the similarity rules can also be applied to a hollow cathode. This has

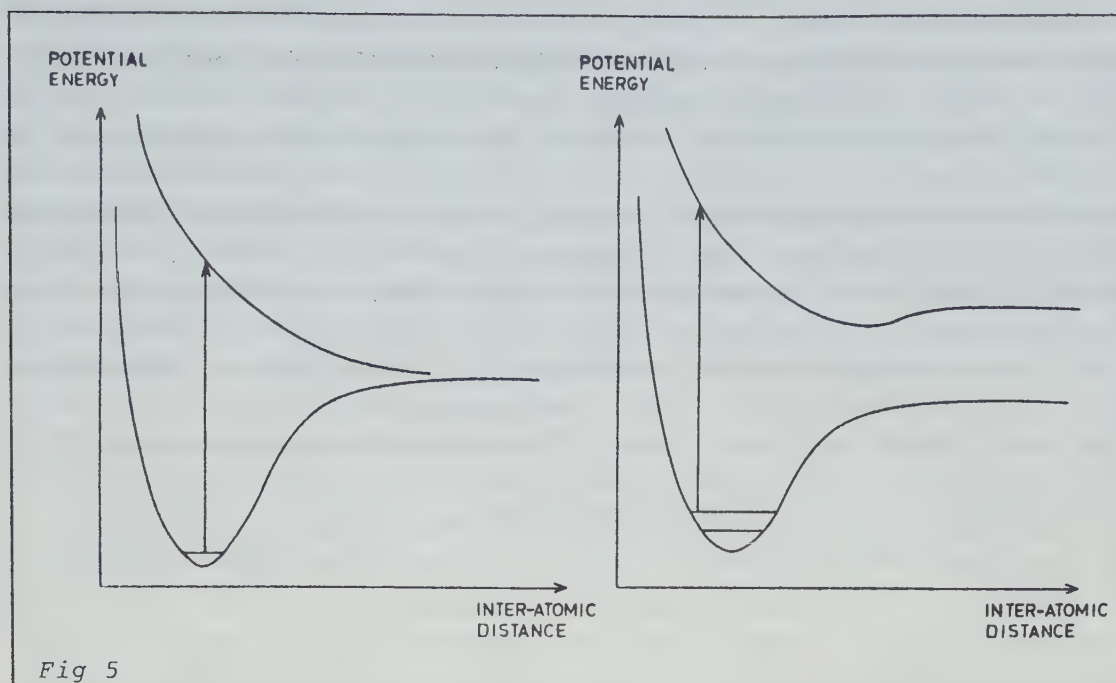
been done previously in making the same type of estimate as here [Lawler *et al.* 1981]. However, it is not clear that these rules apply for the hollow cathode [Pillow 1981]. With the values measured by de Hoog, van Veldhuizen and co-workers [de Hoog *et al.* 1977, van Veldhuizen and de Hoog 1984] and a Ne atom density of $10^{16}/\text{cm}^3$ we obtain metal atom and electron densities of about $10^{11}/\text{cm}^3$ and neon metastable densities [de Hoog *et al.* 1977, Keller and Zalewski 1980] of about $10^{10}/\text{cm}^3$ for our hollow cathode. Calculations by van Veldhuizen and de Hoog [van Veldhuizen and de Hoog 1984] indicate that at currents around 200 mA the metal ion density is about 10% of the electron and carrier gas ion density. All measured and calculated values here refer to measurements and calculations on copper for which the sputtering efficiency is high. In the papers presented in this thesis (paper II, cathode material molybdenum; paper VI, cathode material vanadium) where the sputtering efficiency is lower it is reasonable to assume that the metal atom densities were lower.

Several other well established techniques applicable to similar measurement situations exist, see, e.g. [Büttgenbach 1982] and references therein. Two examples are the "molten ball" technique and the "heat pipe" technique. The molten ball technique [Pendlebury and Ring 1972, Rubinsztein *et al.* 1974] is efficient for evaporating refractory elements. An intense electron beam hits and evaporates the tip of a rod consisting of the material to be investigated. Heating by electron bombardment can be an alternative to the technique of heating described in section A in this chapter. In the heat pipe technique [Vidal and Cooper 1969] the sample is placed in the middle of a cell with windows at two sides. The material is evaporated by heating. The region close to the windows is cooled so that if the evaporated gas drifts towards the windows it will condense on the walls instead of depositing on the cell windows. There is a large variety of discharge techniques for various applications e.g. arc, spark and rf discharge techniques. In some experiments the material sputtered in the hollow cathode effuses into a high-vacuum system through a small hole in the cathode [Duquette *et al.* 1981, Salih and Lawler 1983, Kröll *et al.* 1985, Bergström *et al.* to be published]. This is another possible way of forming an atomic beam of atoms of highly refractory elements.

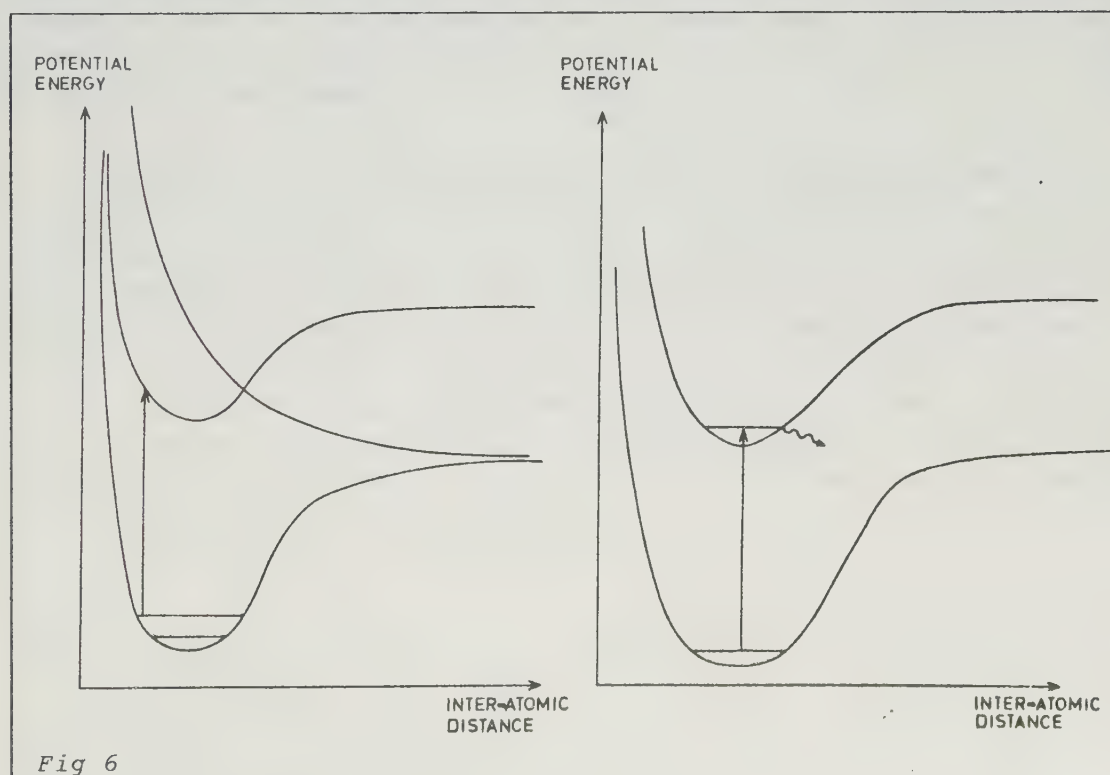
C. Photodissociation

The third method which has been employed for creating free atoms in this work is laser photodissociation of gas phase molecules in which the atom to be studied is one of the constituents. This technique has previously only been used in a few cases [Brewer *et al.* 1982, Das *et al.* 1983] and then only in applications for concentration determination rather than pure spectroscopy.

There is a variety of processes in a molecule which can lead to dissociation after absorption of a photon. The molecule can dissociate immediately after being excited to a repulsive electronic state or a state with only a shallow potential well at large inter-atomic distances (Fig. 5). It may predissociate i.e. an internal rearrangement of the energy in the molecule occurs before the absorbed photon energy is distributed into one bond and breaks it. This can occur e.g. when the excited molecular state potential is crossed by a repulsive state (Fig. 6) or if collisions transfer the molecule from the excited state to the continuum of the



Potential energy diagram showing two pathways for direct photodissociation



Potential energy diagram showing two pathways for predissociation after absorption of a photon. Intersystem crossing (left) and dissociation into the continuum (right).

ground state. Normally only one bond in the molecule is broken during the photodissociation process. However, for polyatomic molecules the molecule may rearrange its internal structure (molecular detachment) during the dissociation. An example for a triatomic molecule is $\text{H}_2\text{O} + \text{photon} \longrightarrow \text{H}_2 + \text{O}$.

As for atomic transitions in general, there are, in the photodissociation process, certain selection rules which restrict the possible combinations of symmetries and multiplicities for the wave functions of the initial molecule and the dissociation products. Thus dissociation may not occur even if the photon energy is larger than the molecular binding energy. Data on photodissociation such as photo-absorption cross sections, quantum efficiencies and on-set wavelengths for various dissociation channels can be found for a large number of molecules in e.g. a book by Okabe [Okabe 1978]. Other general discussions of the photodissociation process are given in Refs. [Calvert and Pitts 1966, Wayne 1970]. Photodissociation is also further discussed in connection with paper V.

IV ELIMINATION OF THE DOPPLER WIDTH

A major complication when probing the interaction between the electron cloud and the atomic nucleus by hyperfine structure or isotope shift measurements is that the Doppler broadening of the atomic transition at room temperatures, in many cases, is of the same order of magnitude as the shifts due to the electron-nucleus interaction. To overcome this complication a large variety of different laser spectroscopic techniques have been developed for various measurement situations. Some more commonly used techniques will be described here with a special emphasis on saturation spectroscopy techniques. A recent survey of Doppler-free spectroscopy can be found in the proceedings of ICAP 1982 [Hänsch 1983].

A. The collimated atomic beam

A particularly straightforward method of eliminating Doppler broadening is to produce a collimated atomic beam (e.g. with the technique presented in chapter III, section A) and let the laser beam hit the atomic beam at 90° . The degree of success in eliminating the information-obscuring Doppler broadening with this technique depends on the collimation ratio (i.e. the ratio of the atomic velocities along the beam to their velocities perpendicular to the beam) that is obtained.

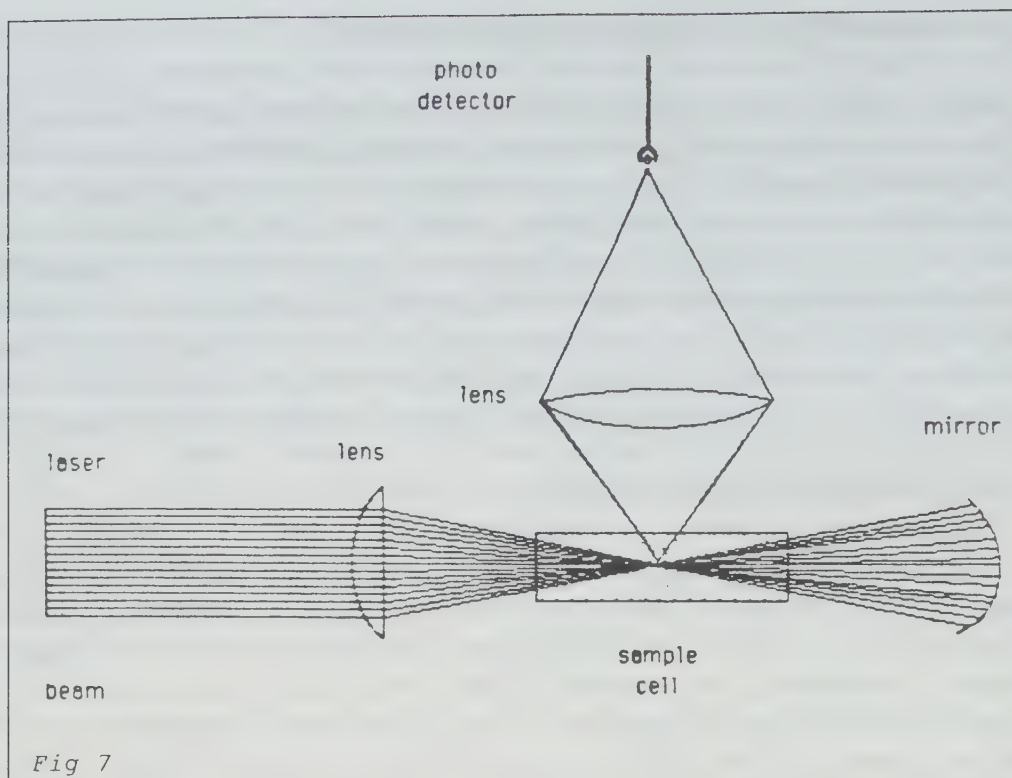
The first order Doppler shift is $\Delta\nu = \nu_0(v/c)$, where $\Delta\nu$ is the frequency shift of the transition, ν_0 the frequency of the transition for an atom with zero velocity parallel to the beam, c the velocity of light in the medium and v the atomic velocity parallel to the laser beam. For a Doppler profile of about 1 GHz a collimation ratio of 100 will reduce the recorded width to about 10 MHz.

B. Two-photon absorption

Doppler-free two-photon absorption was first theoretically predicted by Chebotayev and co-workers [Vasilenko et al. 1970] and was soon experimentally verified by two groups more or less simultaneously [Biraben et al. 1974, Levenson and Bloembergen 1974]. It can be conveniently applied to measurements in a cell or a heat pipe. A typical experimental set-up is shown in Fig. 7. The laser beam is focused in a cell. The laser beam passing the cell is reflected in the mirror which focuses the returning beam at the same spot in the cell. If an atom in the initial state $|i\rangle$ moving at velocity $\mathbf{v}$ absorbs one photon with energy E_i (frequency ν and wave vector $\mathbf{k}$) from each direction it will be left with an energy

$$E_i + h\nu[1+(\mathbf{v}\cdot\mathbf{k})/ck] + h\nu[1-(\mathbf{v}\cdot\mathbf{k})/ck] = E_i + 2h\nu$$

where $k = |\mathbf{k}|$. The upper state will only be populated if $E_i + 2h\nu = E_f$ (E_f is the energy of the final state). We see from the equation above that all atoms, irrespective of their velocity, will contribute to the Doppler-free signal. However, there will also be a Doppler-broadened background due to processes where two photons are absorbed from the same direction.



A set-up for a Doppler-free two-photon absorption experiment. The mirror on the right-hand side reflects the beam back into the sample and focuses it such that the incoming and reflected beams have their focii at the same point. This volume is then imaged on the optical detection system.

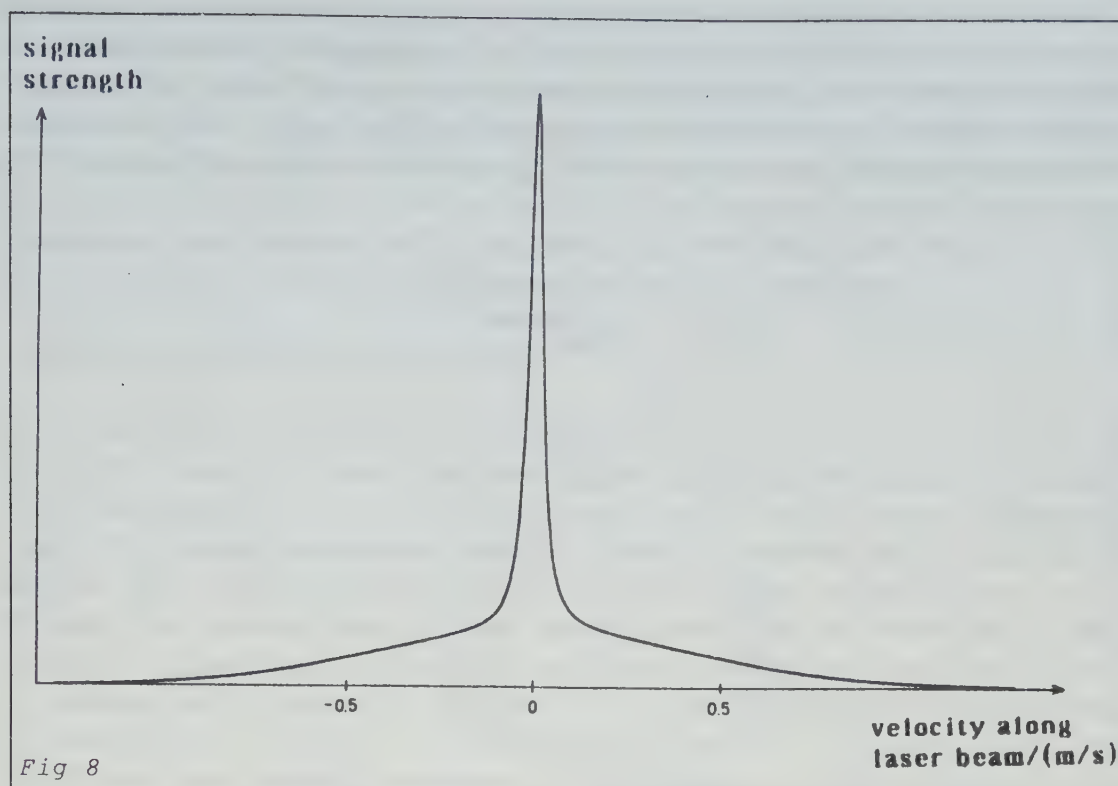
$$E_i + 2h\nu[1 + (\mathbf{v} \cdot \mathbf{k})/ck]$$

$$E_i + 2h\nu[1 - (\mathbf{v} \cdot \mathbf{k})/ck]$$

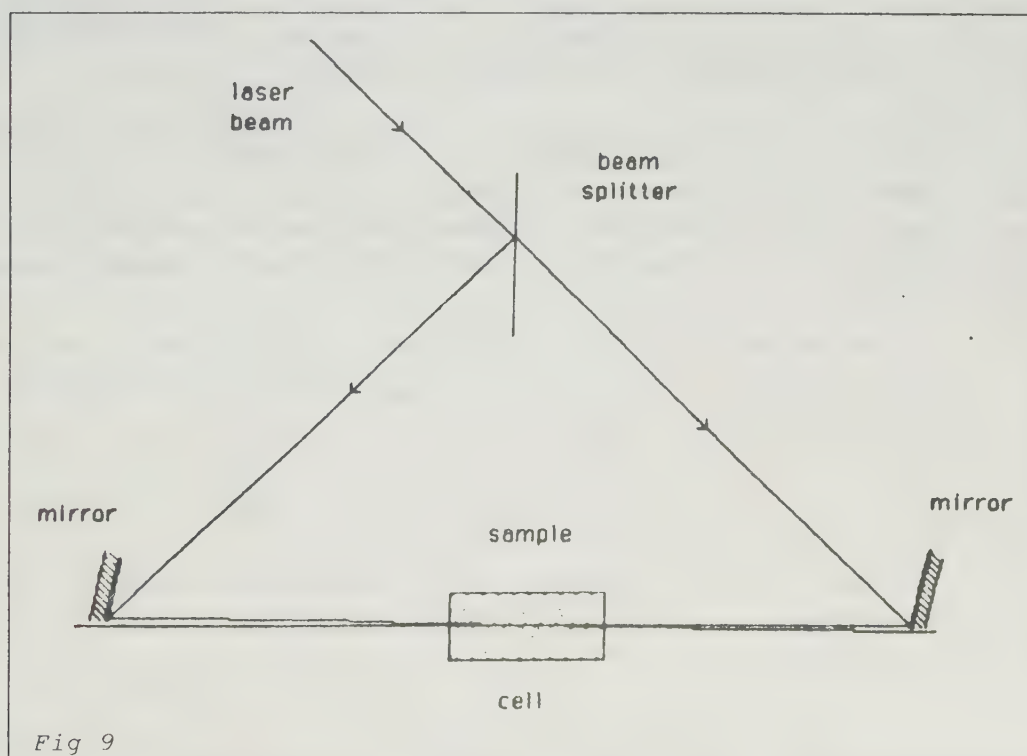
In some cases this can be avoided by choosing the polarizations of the two beams such that the selection rules for transitions from the lower to the higher state only can be fulfilled if one photon from each beam is absorbed [e.g. Demtröder 1982, p. 530]. The background generally presents no great problem since the Doppler-broadened signal is spread out over a large frequency interval while the equally strong Doppler-free signal is narrow-band (see Fig. 8). The drawback of the technique is that the low transition probability of nonresonant two-photon processes compared with allowed one-photon processes may cause the Doppler-free signal to be quite weak although all atoms in the lower state contribute irrespective of their velocity.

C. Saturation spectroscopy techniques

In these techniques the beam from a narrow-band tunable laser (for commercial single-mode dye lasers the linewidth is typically specified to be 1 MHz) is split into two beams which propagate through the sample in opposite directions (see Fig. 9).

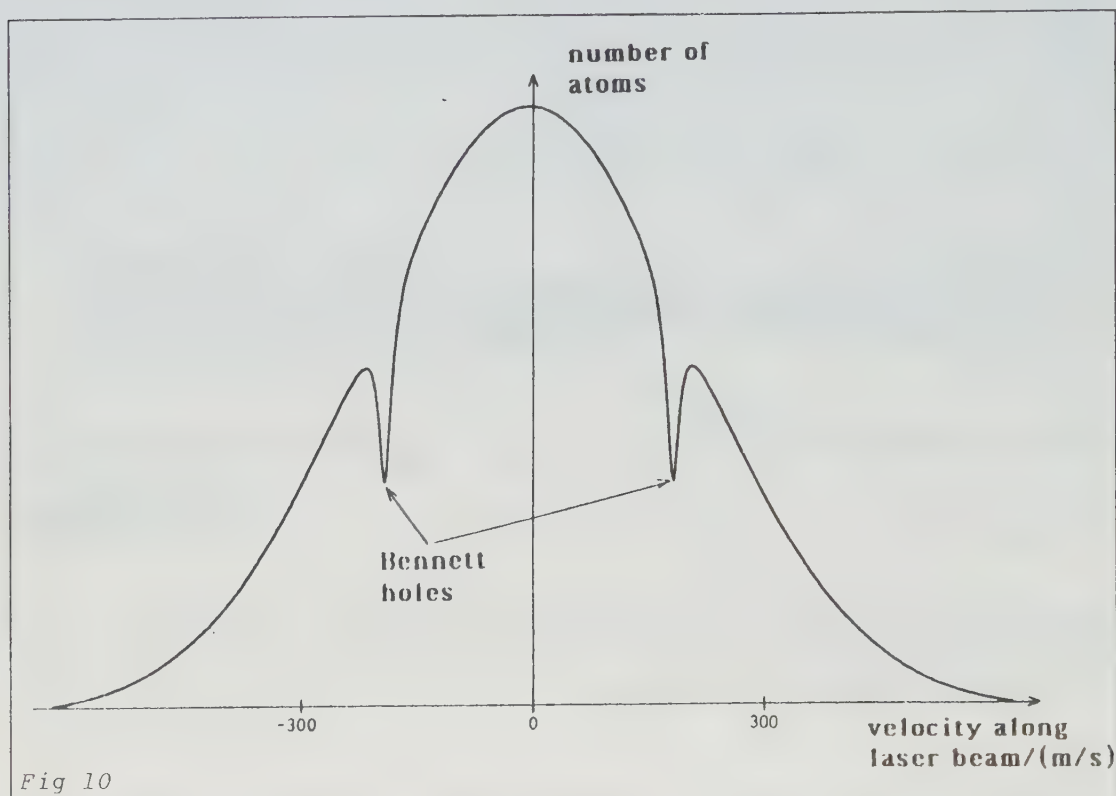


A computer simulation of a Doppler-free lorentzian two-photon signal on its Doppler-broadened gaussian background. The background is here exaggerated by a factor of five.



The figure shows the principle for an experimental set-up of the saturated absorption type.

If the laser is tuned within the Doppler width of a transition the two beams will (since they are narrow-band) each drive the investigated transition only for a specific velocity range. Choosing a specific transition and looking at the atomic velocities parallel to the laser beams the two velocity groups which are excited will lie symmetrically around the velocity group with zero velocity parallel to the laser beams (see Fig. 10).



This figure shows the number of atoms in the lower level as a function of their velocity component parallel to the laser beams. Two velocity groups, symmetrically situated with respect to the group of atoms with zero velocity along the laser beams, are excited. The dips in the population profile arising from the laser-atom interaction are called Bennett holes.

The interaction with the laser light will change the absorption coefficient and refractive index for the excited velocity group. As the laser is tuned to the line-centre frequency both laser beams interact with the velocity group with zero velocity along the laser beams. The absorption in the sample in this situation is different from the situation when the two beams interact with different velocity groups. There are various ways to detect at which frequency this occurs and some of these will be described. Many of these techniques have been developed by Schawlow, Hänsch and co-workers at Stanford e.g. intermodulated fluorescence spectroscopy [Sorem and Schawlow 1972], polarization spectroscopy [Wieman and Hänsch 1976], intermodulated optogalvanic spectroscopy [Lawler et al. 1979] and polarization intermodulated excitation spectroscopy [Hänsch et al. 1981]. New techniques are also being developed [Duffey et al. 1985, Svanberg et al. 1986]. In the first of these two latter papers the saturation induced by the pump beam is modulated by spatially moving the pump beam to and from the overlap with the probe beam and in

the second paper the probe beam is normally completely absorbed in the sample. A counter-propagating pump beam can, however, make the sample more transparent to the probe beam if it interacts with the same velocity group. The probe beam is then transmitted and the recorded signal can be quite strong. Other interesting techniques utilizing the saturation in the medium have been demonstrated but have so far not been extensively employed. E.g. in a paper by Couillaud and Ducasse [Couillaud and Ducasse 1975] the change of refractive index induced by the saturating beam is used to deflect the probe beam at resonance.

1. Saturated absorption spectroscopy

In saturated absorption spectroscopy [Bordé 1970, Hänsch et al. 1971] the two beams are crossed at a small angle and brought to overlap in the sample. One beam, the saturating beam, is an order of magnitude stronger than the counter-propagating beam. The counter-propagating beam is intensity-modulated and is supposed to saturate the investigated transition for the velocity group with which it interacts. The weaker beam is, after spatial filtering for the elimination of stray light from the pump beam, sent to a photodetector. When the two beams interact with the same velocity group the absorption of the probe beam will be modulated since the pump beam modulates the absorption coefficient for this velocity group. Since this Doppler-free signal is modulated lock-in detection can be used to lift it off the background. To quantify this: the intensity absorbed in a sample (dl) is ($\alpha_{12} \ll 1$)

$$dl = \alpha_{12} l(z) dz \quad (17)$$

α_{12} = the absorption coefficient for the transition $|1\rangle \rightarrow |2\rangle$

$l(z)$ = the intensity as a function of the space coordinate z which runs along the beam direction

dz = the length of the sample along the beam direction

α_{12} is the product of the population difference between states 1 and 2 and the absorption cross section which is frequency-dependent but independent of the radiation intensity. To study the intensity dependence of the absorption let us write down a rate equation for the states $|1\rangle$ and $|2\rangle$. Following [Demtröder 1982, p. 45] we have for steady state,

$$0 = (dN_1/dt) = B_{12}\rho(N_2 - N_1) - R_1N_1 + \sum R_{A1}N_A$$

$$0 = (dN_2/dt) = B_{21}\rho(N_1 - N_2) - R_2N_2 + \sum R_{A2}N_A$$

N_i = the population of the state $|i\rangle$

$B_{12}(B_{21})$ = the Einstein coefficient for absorption (stimulated emission)

R_iN_i = the deexcitation rate of the level $|i\rangle$ including spontaneous emission

$R_{Ai}N_A$ = the population rate of level $|i\rangle$ from level $|A\rangle$

$\rho(\nu)$ = the spectral energy density of the radiation field as defined in

chapter II section D. The summation is performed over all states $|A\rangle$ in the atom except $|1\rangle$ and $|2\rangle$.

Solving the equation system above to get $\Delta N = N_1 - N_2$ as a function of the spectral energy density gives

$$\Delta N(\rho) = \Delta N(\rho=0)/[1+B_{12}\rho(R_1^{-1} + R_2^{-1})]$$

Thus, the absorption coefficient as a function of the laser intensity at frequency ν , $I(\nu)$, can be written

$$\alpha(I) = \alpha_0/(1+I/I_S), \quad I_S = cR_1R_2/[B_{12}(R_1+R_2)]$$

That is, the larger the Einstein absorption coefficient is the easier it is to saturate the transition. The treatment above is valid for homogeneously broadened lines. For inhomogeneously broadened lines the result is different. For Doppler-broadened transitions the absorption coefficient must be integrated over the Boltzman distribution of velocities. This will give

$$\alpha(I) = \alpha_0/(1+I/I_S)^{-1/2} \quad (18)$$

The signal-to-background ratio (S/B) in saturation spectroscopy defined by the difference in transmitted intensity on and off the line centre divided by the transmitted intensity can be calculated using Eqs. 17 and 18, and assuming that the absorbed intensity dI is much smaller than I and that the intensity of the probe beam is much lower than the pump beam we get for a Doppler-broadened transition

$$S/B = \alpha_0[1-(1+I/I_S)^{-1/2}]L$$

where I here refers to the intensity of the pump beam and L is the length of the sample. In the special case where $I \ll I_S$ we have

$$S/B = \alpha_0 LI/(2I_S)$$

This can be compared with S/B ratios obtained with other techniques.

2. Intermodulated fluorescence spectroscopy

In this case both beams should preferably have the same strength and they are modulated at two different frequencies. Since the absorption coefficient depends on the incident intensity in a non-linear fashion (Eq. 18) a signal will appear at the sum and difference frequencies when both beams modulate the absorption coefficient for the same velocity group. If we, as in the last section, look at the signal-to-background ratio if none of the beams is modulated and assume that both beams have equal intensity and that $I \ll I_S$ we get

$$S/B = 1/(2I_S)$$

That is, the signal-to-background ratio is independent of the absorbed intensity. Background from spontaneous emission has not been taken into account here.

3. Polarization spectroscopy

In this technique polarized laser beams are employed. The saturating beam can be either linearly or circularly polarized. If it is linearly polarized the polarization of the probe beam is chosen to be linear at 45° to the pump beam. If the pump beam is circularly polarized the probe beam is chosen to be linearly polarized. In both cases the probe beam is linearly polarized before passing the sample. It then encounters a second polarizer set at 90° with respect to the first one. Unless the state of polarization of this beam is changed in the interaction with the sample (or other optical components, cell windows, lenses, etc.) no light will be transmitted through the second polarizer (in practice the polarizers have only a finite extinction). However, the polarized pump beam will induce a nonuniform population among the magnetic sublevels in the upper and lower states. The orientation or alignment (orientation – unequal population in the magnetic sublevels; alignment – unequal population in the magnetic sublevels, however, states with the same absolute value of the magnetic quantum number (M) have equal population) of the atomic angular momentum will rotate the plane of polarization of the probe beam and, in addition, with e.g. a right-hand circularly polarized pump beam (let us denote the right-hand circularly polarized photons in this beam σ^+ in the reference system of the atom) the number of σ^- photons absorbed from the probe beam will be larger than the number of absorbed σ^+ photons. For the probe beam travelling in the opposite direction, σ^- in the reference system of the atom corresponds to right-hand circular polarization while σ^+ corresponds to left-hand circular polarization. In practice the state of polarization is not only changed in the interaction with the atomic sample but also during the propagation through the optical components along the beam. The windows in the device enclosing the sample are normally slightly birefringent. This birefringence is mainly caused by the pressure gradient across the windows (the atomic sample is generally kept at low pressures). If the changes in refractive index were uniform over the area irradiated by the beam it would be possible to compensate for these by inserting an optical device reconstructing the original state of polarization. However, since the changes are not uniform over the beam area this procedure can only be partly effective. To minimize the effect of birefringence in the cell windows it is possible to focus the beam at the entrance and exit windows but two lenses are then needed inside the cell.

The intensity transmitted through the second polarizer (I_t) for a circularly polarized pump beam can be shown to be (for $\theta < 1$)

$$I_t = I_0 [\xi + \theta^2 + b^2 - (1/2)\theta\Delta\alpha_0 Lx/(1+x^2) + (1/2)b\Delta\alpha_0 L/(1+x^2) + (1/4)(\Delta\alpha_0 L)^2/(1+x^2)]$$

I_0 = the incident probe beam intensity

ξ = the extinction ratio of the polarizers

$90-\theta$ = the angle between the settings of the polarizers

b = the birefringence induced by the cell windows

$\Delta\alpha_0$ = the difference in absorption coefficient between the left-hand and the right-hand circularly polarized light at the line centre ($\omega=\omega_0$)

L = the absorption pathlength

$x = (\omega_0 - \omega)/\gamma$

ω_0 = the resonance frequency of the investigated transition

ω = the laser frequency

γ = the natural linewidth of the transition

A similar expression can be obtained for a linearly polarized pump beam. As can be seen from the equation above it is possible to get either a lorentzian shape of the signal by having the polarizers crossed at right angles or to obtain a predominantly dispersion-shaped signal by tilting the analyzing polarizer from the perfectly crossed position. The optimum signal-to-background ratio will occur when the polarizers are turned slightly away from the completely crossed position.

4. Intermodulated optogalvanic spectroscopy

This technique is identical to intermodulated fluorescence spectroscopy except that instead of monitoring the laser-induced fluorescence from the sample the current through the discharge is recorded. Fig. 11 shows the principle for detection. Clearly, the technique can be used only on discharges. Both intermodulated optogalvanic spectroscopy and optogalvanic spectroscopy in general are discussed in more detail in chapter VI, section A.

5. POLarization INTERmodulated EXcitation (POLINEX)

Also here there are two counter-propagating beams. The polarization of one beam is modulated between right and left-hand circular polarization and the other beam is circularly polarized, e.g. say right-hand. (An alternative is to send a circularly polarized wave through a rotating linear polarizer and have the counter-propagating wave linearly polarized.) At the line centre the absorbed intensity will be modulated. The right-hand circularly polarized beam will saturate the σ^+ transitions (these transitions would be driven by a left-hand polarized wave for a counter-propagating wave) such that more light will be absorbed from the counter-propagating wave when it is right-hand circularly polarized than left-hand. The modulation can be detected either in the laser-induced fluorescence light or by using optogalvanic detection as was done in paper II. An advantage of POLINEX is that no modulation can be detected except on the line centre. In saturated absorption spectroscopy, for example, light from the pump beam may leak into the photodetector although the probe beam is selected by spatial filtering. This light is then modulated at the lock-in frequency and can cause serious background problems. A suggestion for an experimental set-up for saturated absorption which takes advantage of the POLINEX concept is shown in Fig. 12.

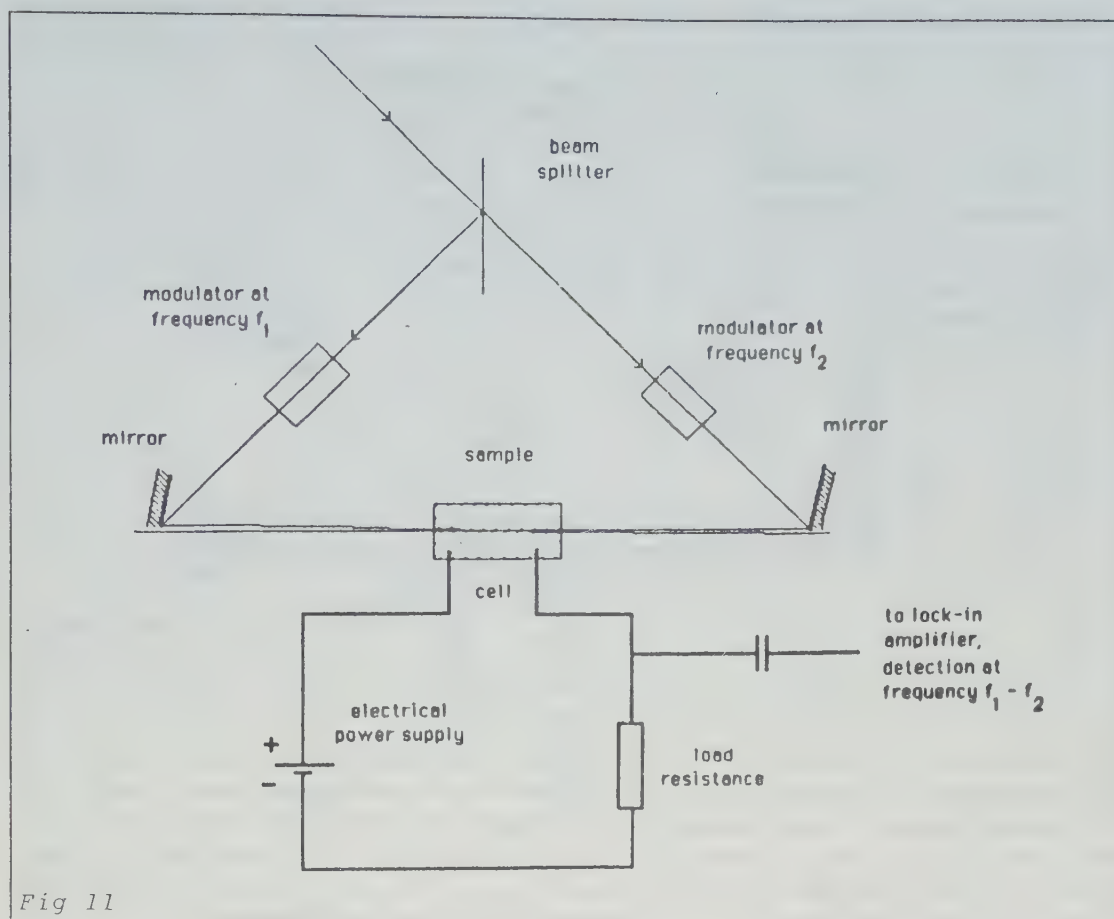


Fig 11

The principle for an intermodulated optogalvanic spectroscopy set-up is shown. A standard saturation spectroscopy type arrangement is used. Both beams are modulated and the non-linear interaction is detected at the intermodulation frequency. A discharge is run in the sample cell. The impedance in the cell depends on the population in the various atomic levels. Thus laser excitation of the atoms in the sample cell will change the current in the circuit. This change in current is detected by measuring voltage changes across the load resistor.

6. Radio-frequency optogalvanic spectroscopy

The technique is identical to optogalvanic spectroscopy except that an rf discharge is used instead of an electric discharge, see Fig. 13. The rf oscillator is driven at low power such that the discharge is close to ceasing. As the laser is tuned to resonance the impedance in the coil and resonance circuit will change and thus the rf power dissipated in the circuit will change. This can be detected as a voltage change over the resonance circuit. POLINEX has also been used in this technique [Lyons et al. 1981]. In Refs. [Bergström 1985, "Progress report 1983-1984" 1985] we have observed that as an alternative to monitoring the voltage across the resonant circuit it is possible to observe frequency changes in the driving rf oscillator.

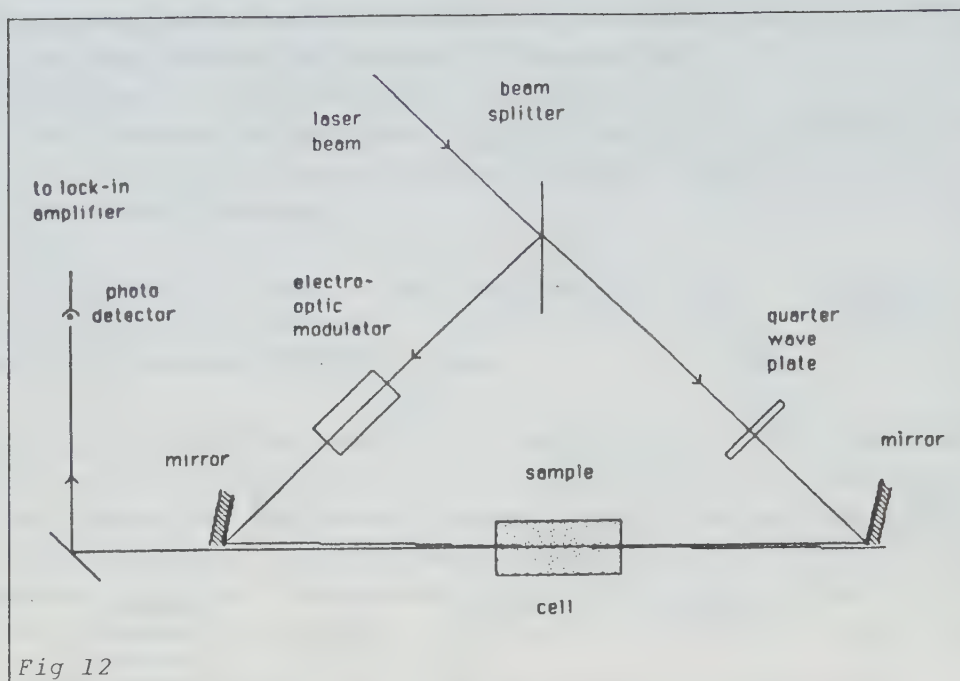
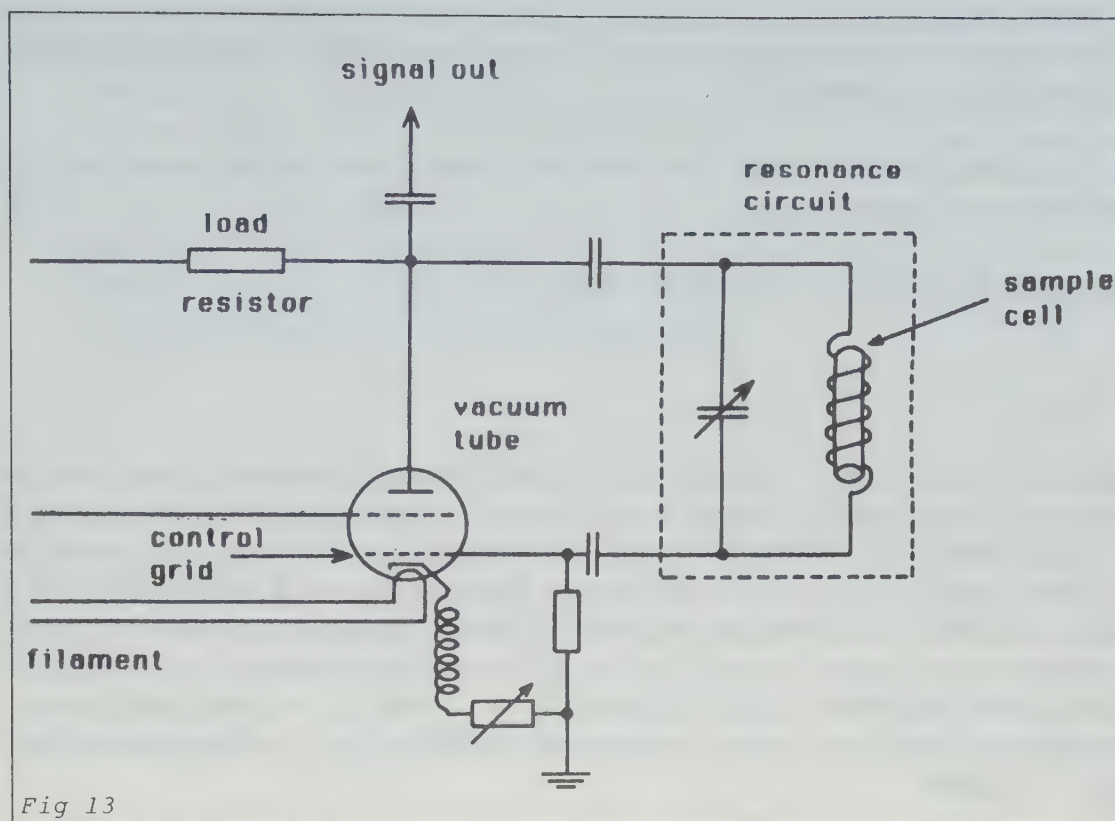


Fig 12

The circularly polarized probe wave impinges on the photodetector after passing the sample cell. The counter-propagating pump wave is modulated between right- and left-hand circular polarization. The advantage of this set-up over ordinary saturation spectroscopy is that reflected pump beam light recorded by the photodetector is not intensity-modulated and thus cannot give a background at the modulation frequency.

7. Frequency modulation spectroscopy and related techniques

There are a number of high frequency modulation techniques where the laser field is phase-modulated [Hall et al. 1981, Bjorklund 1980, Camy et al. 1982]. If the modulation is not too strong the output from the phase modulator will essentially consist of a wave with the original frequency (ω_c) and two sidebands at $\omega_c \pm \omega_m$. In the technique employed by Hall et al. this light impinges on a detector. There will be an interference at frequency ω_m at the detector surface. Two components arise due to interference between the carrier and the lower and higher sidebands, respectively. These components will have the same amplitude but opposite phase. Thus they will combine to give zero signal at the detector. However, if one of the sidebands is partially absorbed in an interaction with the atomic sample an imbalance will occur between the two components and a signal will occur at frequency ω_m . Doppler-free signals are obtained by using a counter-propagating pump beam which can be tuned to interact with the same velocity groups as the carrier or sidebands of the probe beam. At these high frequencies the dye laser noise (which can often be the main contribution to the noise in the techniques above) is shot-noise limited [Hall et al. 1981, Bjorklund and Levenson 1981] and an excellent signal-to-noise ratio can be obtained.



The resonance circuit is connected to the vacuum tube control grid. If the resonance circuit is balanced laser excitation of the atoms in the cell can disturb this balance. The power dissipated in the resonance circuit increases and the voltage on the control grid goes down. This will increase the vacuum tube impedance. The variations in voltage across the vacuum tube as the laser is tuned to resonance with the sample atoms are detected.

D. Quantum beat spectroscopy

Quantum beat spectroscopy [Dodd and Series 1978, Haroche 1976] is especially suitable for the investigation of small hyperfine (or fine structure or Zeeman) splitting. A spectrally broad pulse is used to excite preferably all hyperfine levels in an upper state. The decay from this upper state to a lower state is then recorded. In most cases any of the hyperfine levels in the lower state can be reached from more than one of the upper hyperfine levels. The time evolution for the total probability amplitude for a decay from the upper hyperfine levels $|u_i\rangle$ to a lower state $|f\rangle$ is proportional to

$$\sum \langle u_i | \epsilon \cdot \mathbf{D} | f \rangle \exp(-\omega_i t)$$

ϵ = the polarization of the emitted photon

ω_i = the transition frequency for the transition $|u_i\rangle \rightarrow |f\rangle$

$\mathbf{D}$ = the dipole operator = $e\mathbf{r}$

t = time

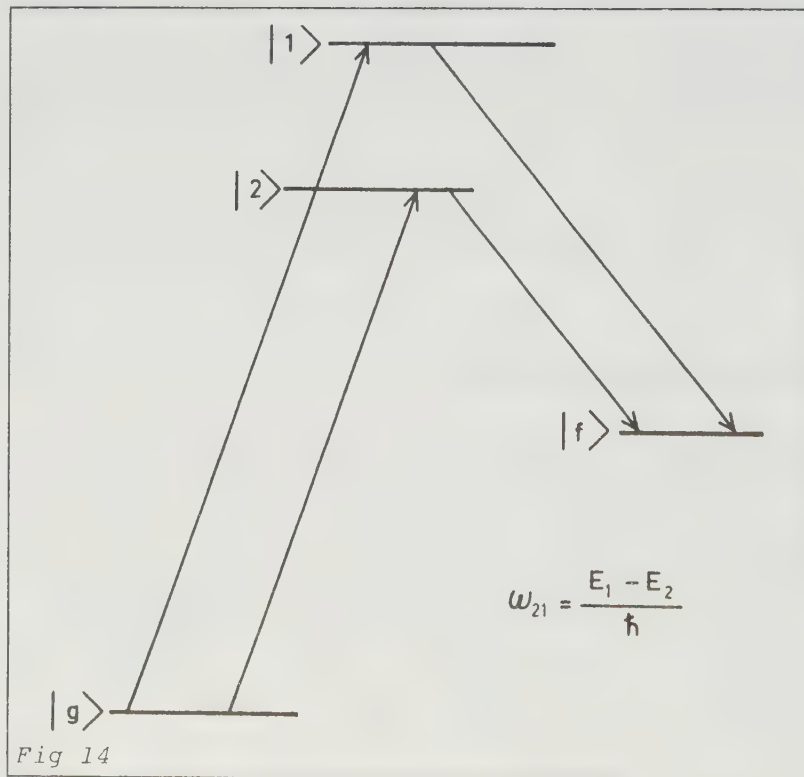
the summation is performed over all states $|u_i\rangle$ which have allowed dipole transitions to the state $|f\rangle$

The recorded intensity ($I(t)$) will then be proportional to the square of the probability amplitude, i.e.

$$I(t) \sim \sum_{u_i} \sum_{u_i'} \langle f_i | \epsilon \cdot \mathbf{D} | u_i' \rangle \langle u_i | \epsilon \cdot \mathbf{D} | f \rangle \exp(-\omega_{ii'} t)$$

$$\omega_{ii'} = \omega_i - \omega_{i'}$$

From the equation above, we can see that there will be oscillations in the recorded intensity at frequency $\omega_{ii'}$, which is the frequency splitting of the upper levels. A less mathematical but perhaps more physical argument is that we can not determine in which state $|u_i\rangle$ the atom was before the emission of a photon thus, as in Young's double-slit experiment, we must add the probability amplitudes for all the possible events before squaring to get the probability intensity. For a situation such as that illustrated in Fig. 14 where $u_1 \rightarrow f$ and $u_2 \rightarrow f$ are both allowed, the exciting pulse must fulfill the following conditions for a strong quantum beat signal to appear.



The atomic states $|1\rangle$ and $|2\rangle$ are coherently excited from the ground state, $|g\rangle$, by a short laser pulse. The modulation frequency ω_{21} in the fluorescence decay to the state $|f\rangle$ is observed.

- 1) The spectral width of the exciting pulse (Γ) must be larger than ω_{21} .
- 2) The duration of the pulse should be considerably shorter than $1/\omega_{21}$ otherwise the decay will contain a sum of oscillating decays. Since these start at different times they will differ in phase and this will wash out the modulation.
- 3) To get an accurate determination of the energy separation, $1/\omega_{21}$ should be much less than τ , the lifetime of the excited state. This makes it possible to record several periods of the modulation frequency before the decay signal becomes too weak to be detected.

V SOURCES OF ERROR

This chapter deals with some general problems that can occur in lifetime and hyperfine structure/isotope-shift measurements of the type performed here, and a discussion of how they may affect the accuracy and reliability of the quantities measured is presented.

A. Lifetime measurements

The quantity we want to obtain is the natural radiative lifetime of the investigated excited state. It should be the unperturbed lifetime in the sense that the recorded lifetime must not be influenced by external fields or collisions. Some mechanisms which, if not properly accounted for, may cause the measured value to be in error will be briefly mentioned. Radiation trapping, pressure broadening and black-body radiation will be discussed. These effects are all relevant for the type of lifetime determination that has been carried out in the papers, that is, experiments where the excited state lifetime is measured by recording the fluorescent decay of atoms excited by resonant pulsed laser radiation.

1. Radiation trapping

If the density of atoms is high, radiation trapping may occur. Radiation trapping (or multiple scattering) is a process in which a photon emitted by a decaying atom is absorbed by another atom and where the detector registers a new photon emitted at the same wavelength by the second atom. This will cause the recorded lifetime to be too long. The probability of reabsorption of a photon is proportional to the transition probability times the density of atoms in the lower state. This means that if we are looking at the decay from a state which has a high oscillator strength for a transition to the ground state the risk of radiation trapping will be especially high. By checking that the measured lifetime remains the same when the pressure is lowered, one can ensure that the measurement is free from radiation trapping. Radiation trapping is further discussed in chapter VI, section B.

2. Pressure broadening

The second effect that may occur at greater pressure is that the atom can be deexcited by collisions before emitting a photon. The process of transferring the excess energy into kinetic or internal energy of a collision partner instead of emitting it as light is called quenching. Quenching will decrease the observed lifetime. The total deexcitation probability from a state $|i\rangle$ can be written [e.g. Demtröder 1982, Eq. 2.82]

$$1/\tau_{\text{eff}} = \sum_k [A_{ik} + \rho(\nu_{ik}) B_{ik} (N_i - N_k g_i/g_k)] + \sum_B N^{(B)} \sigma_{ik}^{(B)} \nu] \quad (19)$$

τ_{eff} = the measured lifetime

A_{ik} = the Einstein coefficient for spontaneous emission

$\rho(\nu_{ik})$ = the energy density of the radiation field at frequency ν_{ik}

B_{ik} = the Einstein coefficient for stimulated emission

N_i = the percentage of atoms/(unit volume) in the state $|i\rangle$

N_k = the percentage of atoms/(unit volume) in the state $|k\rangle$

g_i, g_k = degeneracy factors in the states $|i\rangle$ and $|k\rangle$

σ_{ik} = the collision cross section for transfer $|i\rangle \rightarrow |k\rangle$ at a collision with an atom of type B

$N^{(B)}$ = the number of atoms (molecules) of element B

v = the relative velocity between the two collision partners

The first summation is made over all other states $|k\rangle$ in the atom and the second summation is made over all elements B in the measurement volume.

Let us in the first case assume that $\rho(\nu_{ik})$ can be neglected. I.e., we start to record the decay after the laser pulse has ceased and there is no other radiation field present of significant strength. Let us also assume that there is only one element, denoted B, for which the last term in the equation above is not negligible. We then have

$$1/\tau_{\text{eff}} = \sum A_{ik} + N_B v \sum \sigma_{ik} = 1/\tau + p_B \beta \quad (20)$$

τ = the unperturbed lifetime

p_B = the pressure of element B

$\beta = 1/(kT) v \sum \sigma_{ik}$

The cross section σ_{ik} may also depend on which atomic state the collision partner B is in. (This dependence has been neglected.) From the last equation we see that plotting the inverted measured lifetime as a function of pressure will give the unperturbed lifetime when extrapolated to zero pressure. The slope will give the quenching constant β for the investigated state $|i\rangle$ and collision partner B. This plot is called a Stern-Vollmer plot and was used in the lifetime measurements in paper V.

3. Black-body radiation

Although the effects of collisions can be accounted for it is preferable and often possible to perform the lifetime measurements in a regime where collisions can be neglected during the whole measurement. However there are other effects. Investigating the simplifying assumptions that lead from Eq. 19 to Eq. 20 it turns out that one might need to be careful. There will always be a background field due to black-body radiation (BBR) present in the measurement volume. This field, however, is (at room temperature) very weak at optical frequencies. But, as we go into the infrared region, it will increase in strength. The energy density of the BBR field can, according to Planck's law, be expressed as

$$\rho(\nu, T) = (8\pi h/c^3) \nu^3 / (\exp(h\nu/kT) - 1)$$

It was Gallagher and Cooke who first observed that BBR-induced transitions could affect the lifetimes in excited atomic states quite drastically [Gallagher and Cooke 1979(a), Gallagher and Cooke 1979(b), Cooke and Gallagher 1980]. The induced transition rate (Γ_i^{BB}) is given by [Farley and Wing 1981]

$$\Gamma_i^{BB} \sim \sum_{n_k L_k} \max[L_i, L_k] / (2L_i + 1) (R_{ik})^2 \rho(\nu_{ik}, T) \quad (21)$$

The summation is taken over all final states $|n_k L_k\rangle$

$\max[L_i, L_k] =$ the largest of the values L_i, L_k

$$R_{ik} = \int_0^\infty R_i(r) R_k(r) r^3 dr$$

$R_i, R_k =$ the radial parts of the wave functions Ψ_i, Ψ_k

Γ_i^{BB} will be comparatively large if $|i\rangle$ is a Rydberg state because the BBR field will then induce transitions to nearby Rydberg states. If the frequency for transitions to nearby Rydberg states ν_{ik} lie in the infrared region $\rho(\nu_{ik}, T)$ will be reasonably large. Also, the matrix elements R_{ik} will be large due to the large orbits in the Rydberg states. Eq. 21 has been evaluated by Farley and Wing [Farley and Wing 1981] for hydrogen, helium and the alkali atoms. The induced transition rate will generally peak around $n^* = 10$ with a value of about 10^5 or lower, and at e.g. $n^* = 20$ the transition rate is about a factor of two lower. Clearly these transitions will influence the measured Rydberg state lifetimes if these are in the μs region. Farley and Wing also calculated an upper limit for the black-body-induced transition rate which is

$$\Gamma_{\max}^{BB} = 2 \cdot 10^7 / n^{*2} \quad (\text{unit} = s^{-1})$$

at room temperature. This simple formula only estimates the transition rate but at least it is possible to conclude that if the recorded lifetime is not affected by the transition rate calculated from this equation black-body effects can most likely be neglected. The BBR-induced shortening of Rydberg state lifetimes has also been investigated in our laboratory [Bhatia et al. 1981].

B. Hyperfine measurements

Three types of effects will be briefly mentioned. Shifts in the energy levels due to collisions (pressure shifts), shifts in energy due to static electric fields (DC Stark shifts) and shifts due to interactions with strong electromagnetic fields (AC Stark shifts).

1. Pressure shifts

Pressure broadening was treated earlier in this chapter. To evaluate the pressure shift we may begin by writing the expected intensity from a collision-broadened emission line [Demtröder 1982, p. 91]:

$$I(\nu) = \int A_{ik}(R) P_{\text{col}}(R) [E_i(R) - E_k(R)] dR$$

R = the distance between the two collision partners

P_{col} = the probability per unit time that the distance between the two collision partners lies between R and $R+dR$

$E_i(E_k)$ = is the energy of the initial (final) state

The energies of the states are a function of the distance between the collision partners. If collisions are frequent they will shift position of the line. This effect occurs with charged as well as uncharged particles. For the hollow cathode measurements pressure shifts can be investigated and eliminated by recording the position of the line as a function of carrier gas pressure and extrapolating the line position to zero pressure.

2. DC Stark shifts

The change in energy (ΔE) for a state interacting with a static electric field can be calculated with the operator $H_{\text{int}} = e\mathbf{E} \cdot \sum \mathbf{r}_i$ using second order perturbation theory ($\mathbf{E}$ is the electric field). If the total electronic angular momentum J is a good quantum number one obtains

$$\Delta E = -(1/2)[\alpha_0(\gamma J) + \alpha_2(\gamma J)(3M_J^2 - J(J+1))/(J(2J-1))]E^2$$

ΔE = The shift in energy for the level

M_J = The projection of $\mathbf{J}/(h/2\pi)$ along $\mathbf{E}$

γ = any additional quantum numbers needed to characterize the state

$\alpha_i(\gamma J)$ = the tensor polarizabilities of rank i , as a function of J and γ

We see that an electric field both shifts the position of a line and splits a state (providing $J > 1/2$). Similarly to the way in which pressure shifts are treated, the Stark effect can be eliminated by recording the line positions as a function of electric field strength and extrapolating the line positions to zero electric field. However, as can be seen in Fig 4 the fields are very low in the negative glow region. With the large hollow cathode used in papers II and VI no Stark shifts or Stark splitting have been observed.

3. AC Stark shifts and AC Stark broadening

At the end of this chapter we discuss the influence of a strong laser field on an atomic transition. As can be seen in chapter IV, section C1 the line profile seen by the probe beam in a saturation spectroscopy measurement is broadened by the saturating beam. To briefly discuss this, let us study a two-level system where other relaxation processes than the spontaneous decay of the upper state (here

denoted $|2\rangle$) are absent. From e.g. [Stenholm 1984, chapter 2] we see that if a laser is tuned to a transition $|1\rangle \rightarrow |2\rangle$ the linewidth of the transition (Γ) will be

$$\Gamma = (\gamma^2 + (2\pi\mu E/h)^2)^{1/2}$$

$$\gamma = 1/\tau$$

τ = the lifetime of level $|2\rangle$, it is assumed that $|1\rangle$ is the ground state

E = the electric field strength

$\mu E = \mu \cdot E$, i.e. assuming μ and E have the same direction

$\mu = \langle 1 | e r | 2 \rangle$ is the dipole moment of the transition

$4\pi\mu E/h = \omega_R$ is called the Rabi frequency of the transition and is a measure of how fast the atoms are transferred between the two states under the influence of a resonant electromagnetic field. The time taken to transfer the population from one state to the other is $2\pi/\omega_R$. From the equation above it is clear that the electromagnetic field will broaden the transition. This saturation broadening (or power broadening) will, at least to some extent, be present in the measurements where CW lasers are used. It will, however, not affect lifetime measurements of the type performed in papers III–V since the decay is recorded after the laser pulse has ceased.

A sufficiently strong field will also cause a splitting of a line [e.g. Stenholm 1984, chapter 4]. (This can be pictured as the Rabi frequency is putting sidebands on the laser field [Farley and Wing 1981].) It has several names, dynamic Stark effect, AC Stark effect or Autler–Townes effect [Autler and Townes 1955]. If AC Stark broadening or AC Stark shifts are present in the measurements, they can be compensated for by extrapolating towards lower laser powers.

VI DISCUSSION OF PAPERS

In this chapter the results obtained and presented in the papers are recapitulated and discussed. It also contains information on some computational and technical points which have not been described in detail in the papers.

The papers have been divided into three groups. The first one, consisting of papers II and VI, concerns Doppler-free spectroscopy on discharges. The second one treats lifetime measurements and involves papers IV and V and parts of paper III. The third and last group contains paper I and the rest of paper III which cover hyperfine structure and isotope-shift measurements on Ba using a collimated atomic beam and hyperfine structure measurements on Al using quantum beat spectroscopy, respectively.

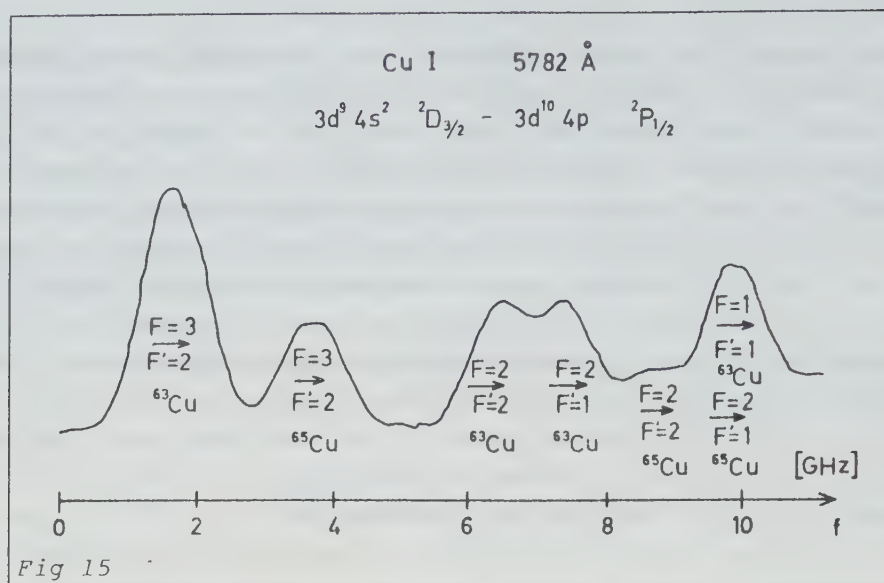
A. Doppler-free spectroscopy on discharges

The aim of the project involving papers II and VI was to initiate and develop a technique suitable for Doppler-free spectroscopy on noble gases and refractory elements. These elements could not easily be investigated using two-step excitation on an atomic beam of the type normally used in our group at that time. I will briefly recapitulate the early steps in the project. Questions which had to be addressed at that time were what type of discharge should be used (designed) and which measurement technique would be the most efficient one. The Stanford group had recently presented their first papers on intermodulated optogalvanic laser spectroscopy [Lawler et al. 1979, Siegel et al. 1981] a technique which seemed to be very promising for the type of measurements we were interested in performing. However, other Doppler-free techniques, such as intermodulated fluorescence spectroscopy and Doppler-free two-photon absorption [Liao et al. 1980, Freeman et al. 1980, Lawler et al. 1979, Biraben et al. 1980] had also been successfully applied to noble gases. In our group fluorescence detection was employed in essentially all measurements and some of our members also had previous experience from polarization spectroscopy [Grafström et al. 1978], but no one in the group had previously worked with optogalvanic spectroscopy.

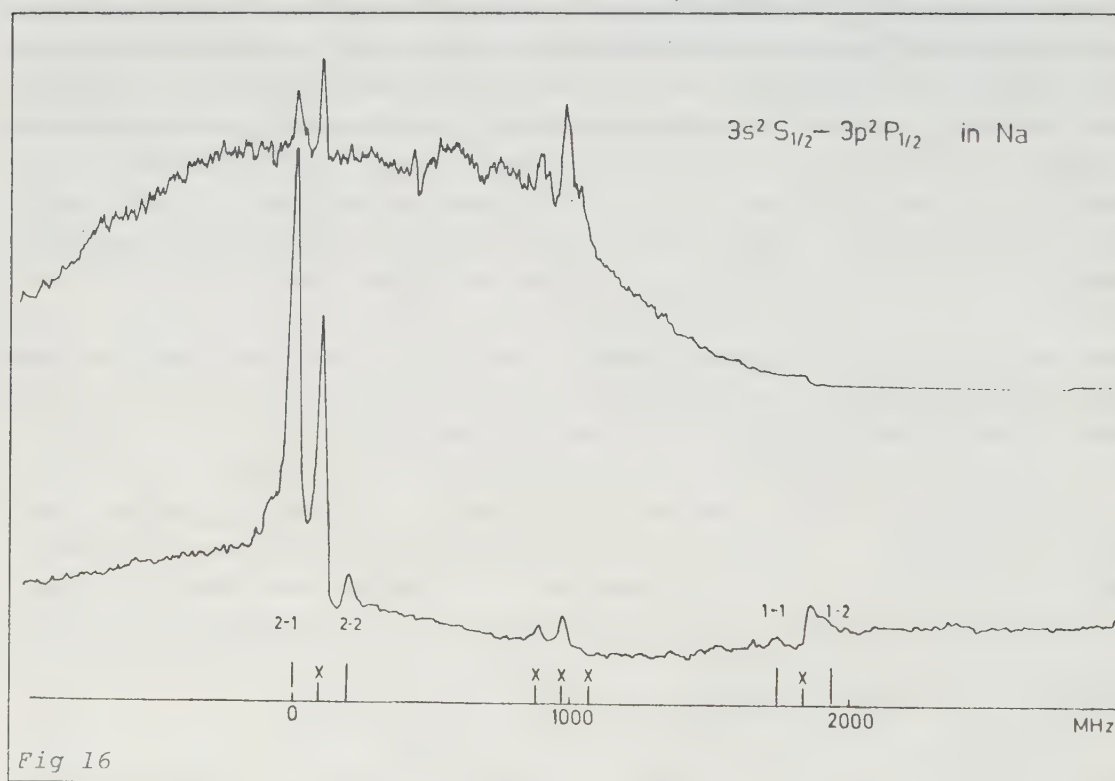
Therefore the project started with a diploma work on optogalvanic laser spectroscopy [Kröll 1981]. After this, broad-band optogalvanic spectroscopy was performed on the He $2p\ ^3P - 4d\ ^3D$ transition in a HeNe laser tube (unpublished) and on copper (Fig. 15). The measurements on copper were performed using a hollow cathode with a 6 mm bore diameter originally designed to study the energy level structure of ionized rare gas atoms.

The linewidths obtained with this hollow cathode were quite large and a new hollow cathode was built using a design by Lawler et al. [Lawler et al. 1981]. This hollow cathode, especially designed for Doppler-free laser spectroscopy, had a large bore diameter (3 cm) such that pressure and Stark broadening would be reduced. The two hollow cathodes were compared regarding linewidths and line

profiles in conjunction with isotope-shift measurements in Ne $3s - 3p$ transitions [Belfrage et al. 1983].

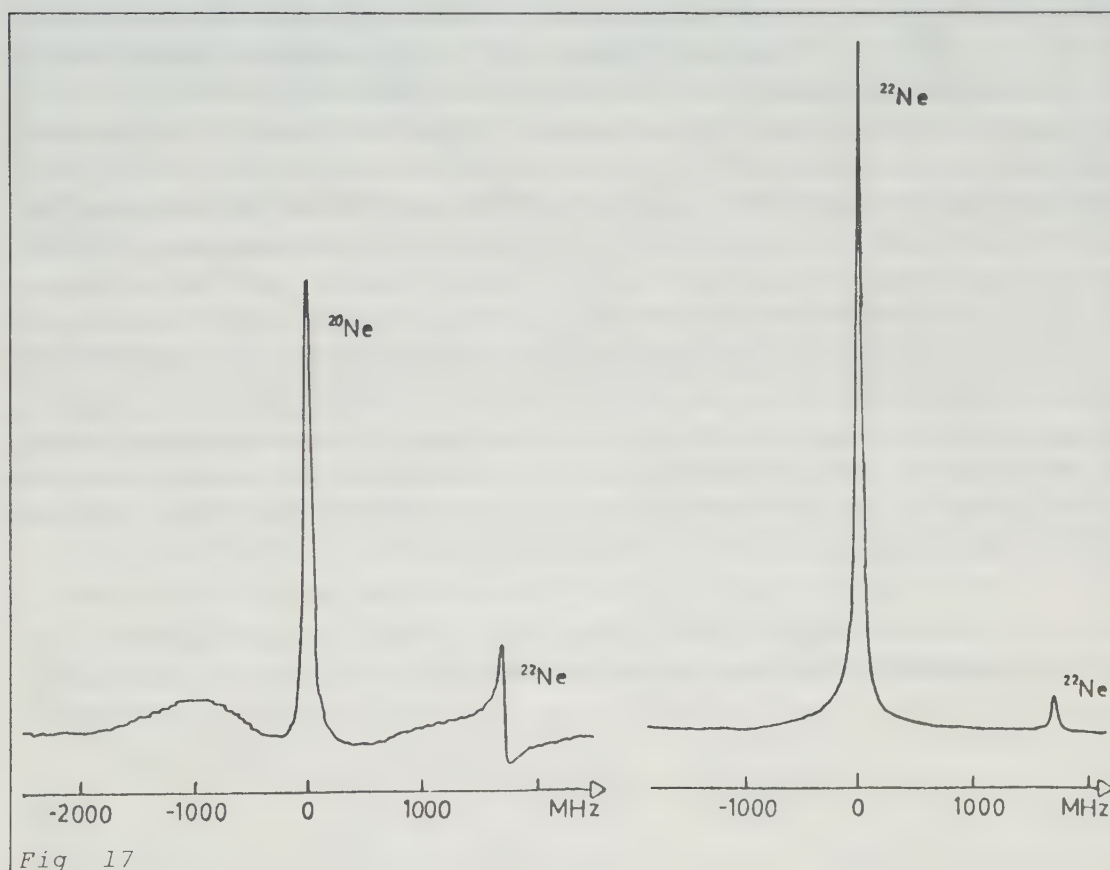


Doppler-limited experimental recording of the $3d^4 4s^2 \ ^2D_{3/2} - 3d^{10} 4p \ ^2P_{1/2}$ transition in copper using optogalvanic detection. The two stable copper isotopes both have nuclear spin $3/2$.



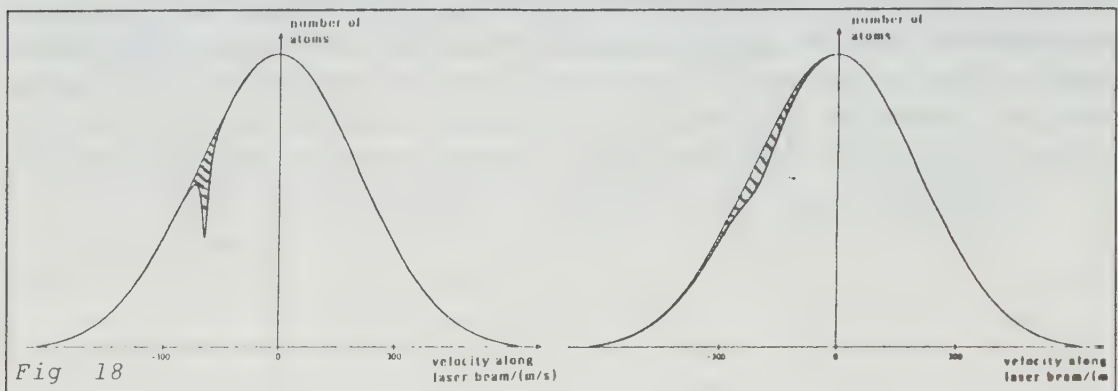
Two experimental polarization spectroscopy recordings of the $3s \ ^2S_{1/2} - 3p \ ^2P_{1/2}$ transition in sodium. In the lower trace the earth's magnetic field has been compensated for leading to a significant improvement in the signal-to-noise ratio.

The new hollow cathode with the large bore gave a factor of 2-3 smaller homogeneous linewidths even when it was run at higher currents and at a higher pressure than the small-bore hollow cathode. The larger linewidths in the small-bore hollow cathode were attributed to Stark broadening due to a less favourable electric field arrangement. The pressure broadening measured for the $3s - 3p$ transitions was in reasonable agreement with values obtained by other investigators. At the currents, pressures and laser intensities used (100-200 mA, 10-100 Pa and 10-100 mW) no evidence of pressure or DC or AC Stark shifts was observed. The linewidths for the Ne transitions in this investigation were about 40 MHz. We also studied the influence of magnetic fields on the Doppler-free signal in polarization spectroscopy (unpublished). Fig. 16 shows that a longitudinal magnetic field gives a Doppler-broadened background. If the propagation of the probe beam through the sample is regarded as the transfer of a wave via oscillating dipoles (i.e. the atoms in the sample) these dipoles will undergo Larmor precession in the magnetic field. There will effectively be a Faraday rotation such that the probe is transmitted through the second polarizer. This effect has been studied in some detail by Gawlik and Series [Gawlik and Series 1979]. Also, a too strong probe beam will distort the line shapes. An example of this is shown in Fig. 17.



Two experimental recordings of the $2p^5 3s \ ^3P_2 - 2p^5 3p \ ^3P_1$ transition in neon at $\lambda = 588 \text{ nm}$ using polarization spectroscopy. The experimental conditions were identical in the two recordings with the exception that the probe beam intensity was about two orders of magnitude higher in the recording on the left. In the recording on the right the probe beam intensity is a few mW/cm^2 .

In paper II, which was presented at the optogalvanic conference in Aussois (1983) [*"International..." 1983*], the four Doppler-free techniques intermodulated fluorescence spectroscopy (IFS) [Sorem and Schawlow 1972], intermodulated optogalvanic spectroscopy (IMOGS) [Lawler et al. 1979], polarization spectroscopy (PS) [Wieman and Hänsch 1976] and polarization intermodulated excitation (POLINEX) [Hänsch et al. 1981, Dabkiewicz and Hänsch 1981] employing optogalvanic detection were compared in studies on the Ne $2p^5 3s \ ^3P_2 - 2p^5 3p \ ^3P_1$ transition at $\lambda = 588$ nm and the Mo $4d^5 5s \ ^5S_2 - 4d^5 5p \ ^5P_3$ transition in Mo at $\lambda = 551$ nm. Doppler-broadened background signals were present at the intermodulation frequency in both the IFS and the IMOGS techniques. To explain why this is the case let us look at Fig. 18.



The left of these computer-generated curves shows the Bennett hole in a velocity distribution. The population corresponding to the shadowed area in the figure is modulated by the exciting laser light. The curve on the right shows the principle of what happens when there are velocity-changing collisions in the discharge. If one velocity group is emptied by the excitation, atoms from other velocity groups are transferred to this group and thus the population in other velocity groups will also be modulated by the laser-atom interaction.

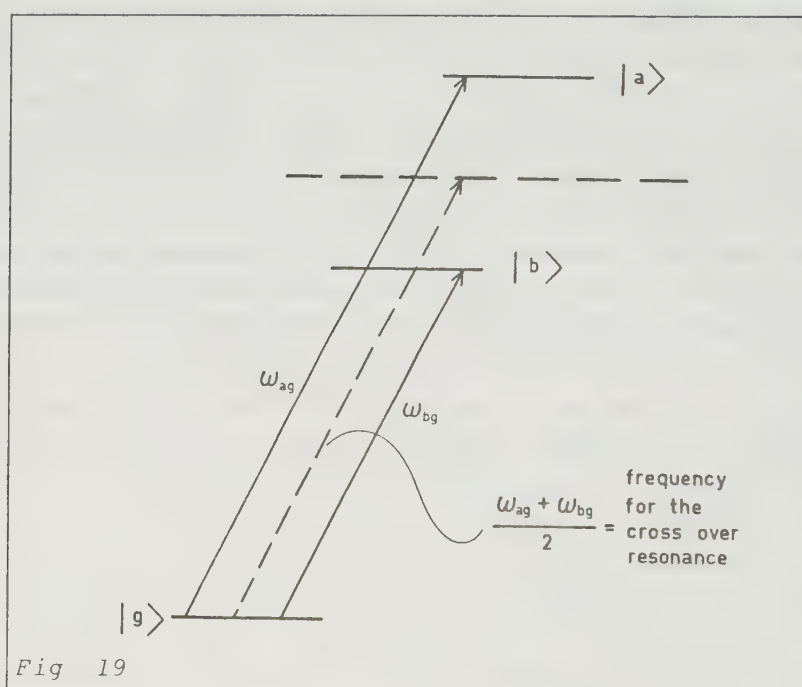
This figure shows the atomic velocity distribution in the lower state and what part of the population is modulated by the saturating beam. A group of atoms with a specific velocity has been transferred to an upper state. Collisions in the plasma will transfer atoms with other velocities to the depopulated velocity group. Thus also the population of atoms in other velocity groups than the one excited will be modulated. Since the transfer of the atoms between different velocity groups has some characteristic time constant this occurs with some delay with respect to the initial excitation. Due to the collisions the population in the majority of the velocity groups will be modulated when the laser drives a transition. Thus a Doppler-broadened background arises. Since this background starts to appear after the collisions it can be separated from the Doppler-free signal by using high-frequency modulation and phase sensitive detection [Aminoff and Pinard 1982].

If the lower state is metastable the effects of these velocity-changing collisions on the line profile depend on the parameter τ_{LL}/τ_{VCC} where τ_{VCC} is the average time between velocity-changing collisions and τ_{LL} is the average time the atom spends in the metastable state. As discussed by e.g. Lawler et al. [Lawler et al. 1981] the time associated with changing the velocity of the atoms can be increased by running the discharge at higher currents and lower pressures. A lower pressure will decrease the collision frequency and at a higher current there will be more inelastic electron-atom collisions. These will deexcite the metastable atoms and thus shorten the effective lifetime in the metastable level. In this way the Doppler-free signal can be enhanced with respect to the Doppler-broadened one. However, as also pointed out by Lawler et al. the tendency to deposit cathode material on the cathode walls and windows increases under these operating conditions. This is particularly unattractive in optogalvanic detection since leakage currents going from the anode to the cathode along the deposited material will increase the electrical noise in the discharge [Warner, private communication]. Techniques like polarization spectroscopy and POLINEX, which not only probe the population but also the orientation of the atoms in the sample, are not so sensitive to velocity-changing collisions since the orientation is normally destroyed for the participating atoms. Consequently, these atoms contribute neither to the Doppler-broadened nor to the Doppler-free signal.

The ratio between the Doppler-free and the Doppler-broadened peak was higher in the IFS than in the IMOGS measurements. To see what this implies let us first conclude that the absolute signal strength in IFS is determined by properties like the collection efficiency of the detection system, the beam overlap, the beam intensity, the quantum efficiency of the photomultiplier, line strength and population in the different atomic levels, the angular distribution of the fluorescence light and the quenching rate. The relative strength between the Doppler-free and Doppler-limited signal depends on to what extent the velocity-changing collisions modulate the level populations, but not on any of the other parameters listed above. The signal strength in IMOGS depends on the line strength, the atomic population, the beam overlap, the beam intensity, the number of created electrons (ions) per absorbed photon, the collection efficiency in the discharge i.e. how many of the created electrons (ions) actually reach the anode (cathode) before recombining and the electric/electronic detection system. The ratio between the Doppler-free and Doppler-broadened signal depends not only on the redistribution between the velocity groups caused by velocity-changing collisions, but also on the discharge processes.

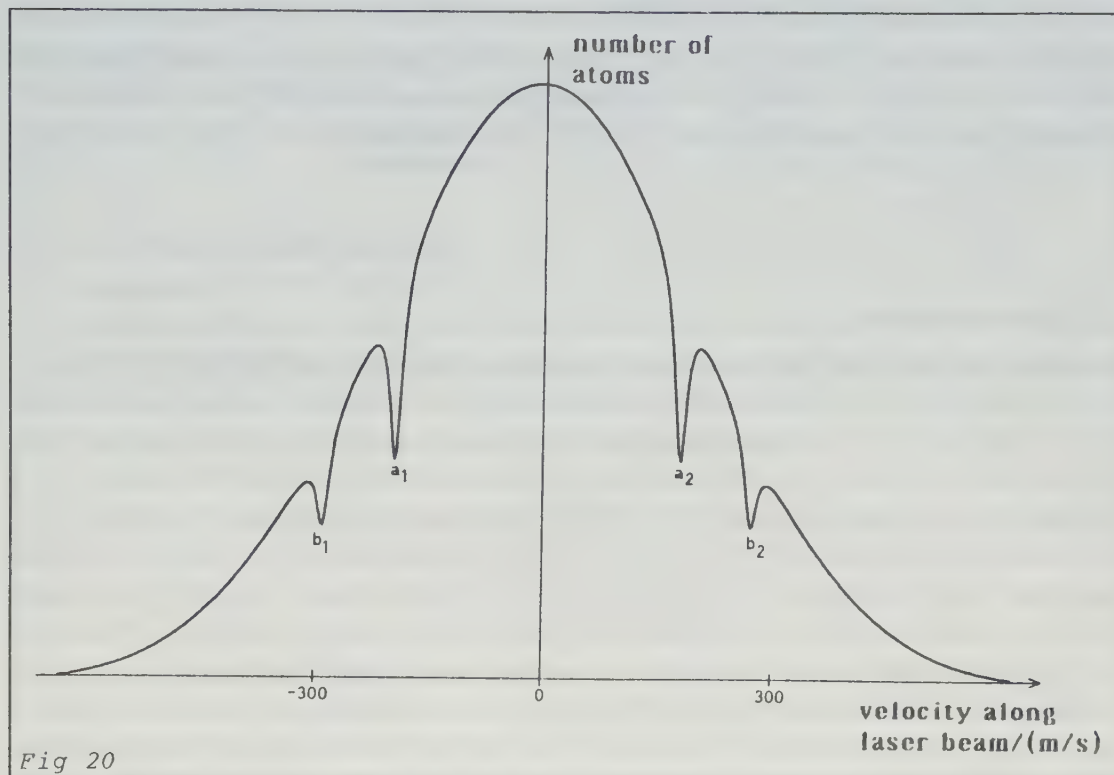
To check if the hypothesis that processes in the discharge can be responsible for producing a Doppler-broadened background at the intermodulation frequency in IMOGS is reasonable, let us look at how the signal arises in the optogalvanic technique. The conference proceedings from the optogalvanic conference in Aussois, summer 1983 ["International..." 1983], contains most pertinent information on optogalvanic spectroscopy up to that date. Various aspects of the mechanism for the optogalvanic signals in hollow-cathode or similar discharges have, for some years, been discussed quite extensively in the literature [e.g. Keller et al. 1983, Shuker et al. 1983, Lawler and Doughty 1983, Hameau et al. 1985, van de Weijer and Cremers 1985, Valentini 1985]. Different contributions to the change in cur-

rent induced by the absorption of light can be found [Keller et al 1983]. However, one of the dominating processes is the deexcitation of laser-excited atoms in superelastic electron-atom collisions [Drèze et al. 1982, Gagné et al. 1983 (in french), Keller et al. 1983]. These collisions raise the electron temperature in the discharge and thus increase the rate of ionization of atoms in the discharge. To visualize how a Doppler-broadened signal can arise at the intermodulation frequency let us, for simplicity, assume that one beam modulates the electron temperature in the discharge at frequency f_1 and the other beam, modulated at frequency f_2 , excites atoms. The probability of ionization is higher both for an excited atom and when the electron temperature in the plasma is higher. It is intuitively most likely that these two effects will add in a non-linear way when contributing to the optogalvanic signal. If this is the case, a signal will arise at the intermodulation frequency irrespective of which velocity group is excited. The chopper, the chopper frequency and the lock-in amplifier were the same in the IMOGS and IFS measurements. Improper use or malfunction of these can affect the ratio between the peaks, but since the same equipment was used in both the IMOGS and IFS measurements both methods should be affected in the same way. The implication of the discussion above is that the discharge processes induce Doppler-broadened background signals on the intermodulation frequency in IMOGS. Since the detection limit for the Doppler-free signal in both techniques mentioned above is set by fluctuations in the broad-band background pedestal, Doppler-broadened signals at the intermodulation frequency are definitely disadvantageous.



For a saturation spectroscopy experiment the energy level diagram above will give a so-called hole burning in the velocity distribution as depicted in Fig. 20. The frequency of the cross-over resonance corresponds to a transition from the lower state to a state lying in between the two upper states.

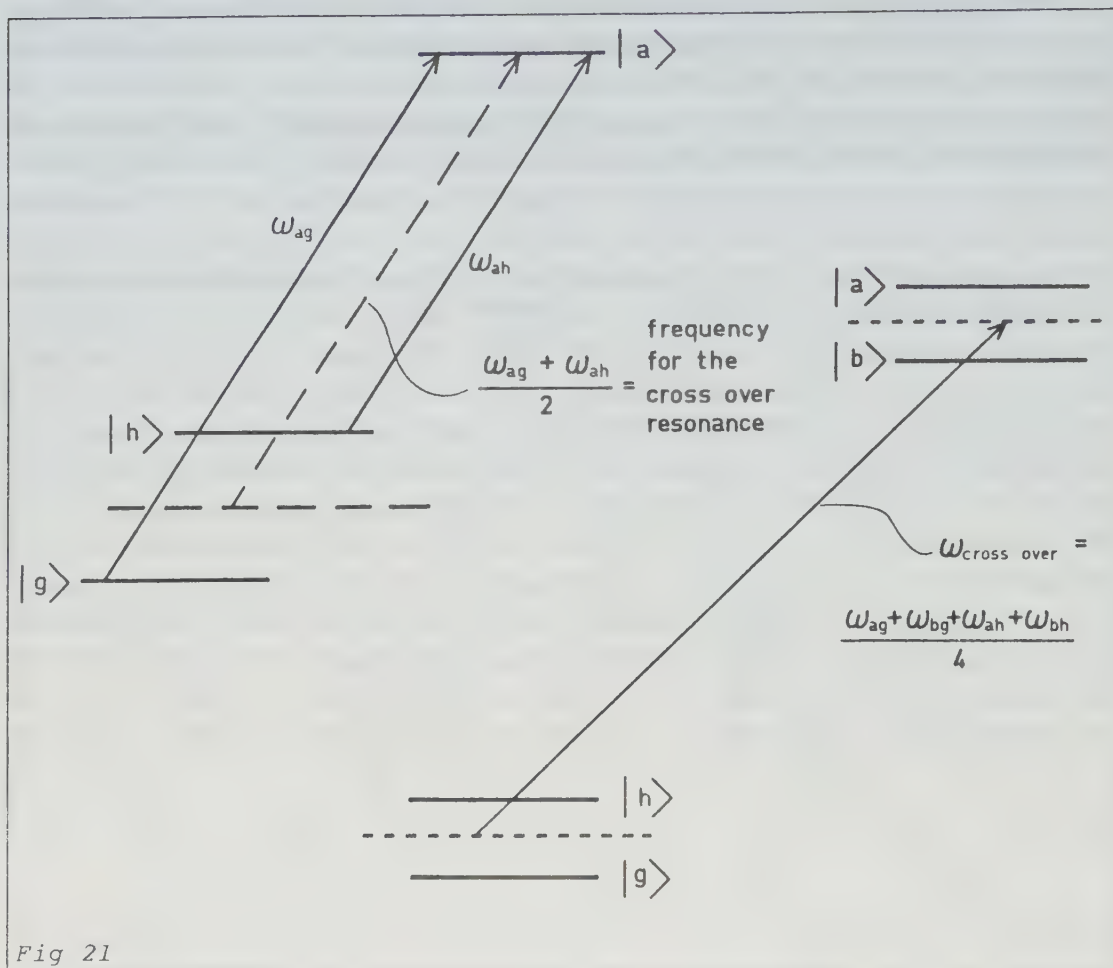
In all the methods mentioned above, the recorded spectra contain additional lines in addition to the real transitions. These are so-called cross-over resonances, and can be explained with the help of Fig. 19. "a" and "b" are two energy levels separated, let us say, 100 MHz in frequency. If this transition is probed in a saturation spectroscopy experiment there will be hole burning effects in the velocity ensemble as depicted in Fig. 20.



Hole burning in a velocity ensemble arising from the excitation scheme in figure 19. The letters a and b refer to hole burning due to excitation to levels a and b respectively. The indices 1 and 2 refer to excitation by the two counter-propagating laser beams.

The indices 1 and 2 in the figure refer to excitation by the two counter-propagating laser beams, and a and b denote hole burning due to excitation to the levels a and b in Fig. 19. When the laser frequency is tuned towards the line centre the holes in the Doppler profile above will overlap at three points. First the holes a_1 and a_2 will overlap. This corresponds to transition a. Scanning the laser another 50 MHz will make b_1 and a_2 as well as a_1 and b_2 overlap. Finally, scanning another 50 MHz will tune the laser to transition b, and b_1 and b_2 will overlap. Evidently, a signal is recorded between the two signals corresponding to the real transitions a and b. In a cross-over resonance the two counter-propagating laser beams interact with the same velocity group but, the two beams drive two different transitions for the atoms in this velocity group. For the case illustrated in Fig. 19 we have a cross-over resonance with a common lower level. For cross-over resonances to appear the separation between the levels must be less

than the Doppler width. Other types of cross-over resonances, which e.g. were observed in paper VI, are depicted in the energy level diagrams below (Fig. 21).



This figure shows two additional energy level diagrams which would give cross-over resonances in a saturation spectroscopy experiment provided the splitting between the levels a and b and between the levels g and h is smaller than the Doppler-width.

The cross-over resonances can in principle be an aid for identifying spectra but normally they only make the analysis of the recorded spectra more complicated. One way to eliminate the cross-over resonances is to use a third laser beam (from another laser) to mark the velocity group moving perpendicular to the two counter-propagating laser beams in the saturation spectroscopy experiment as has been done by Neukammer et al. [Neukammer et al. 1981].

Optical pumping between the different hyperfine levels can, especially in polarization spectroscopy, affect the signal strengths and distort line profiles drastically. For identification of spectra the intensity within a hyperfine array can be obtained from e.g. Kopfermann [Kopfermann 1958, table 2]. Coefficients which describe the birefringence and dichroism induced by the optical pumping in polarization spectroscopy can be found in e.g. Refs. [Dabkiewicz and Hänsch 1981, Teets et al. 1977]. General treatments of line profiles and signal strengths in saturation spectroscopy techniques can be found in Refs. [Nakayama 1984(a), Nakayama 1984(b), Nakayama et al. 1980, Nakayama 1981].

In paper VI we varied the modulation frequency in order to reduce or eliminate the Doppler-broadened background superimposed on the Doppler-free signal. A high modulation frequency gave a better discrimination of the background noise. This was expected since the dye laser noise within a certain bandwidth decreases with increasing frequency. High modulation frequencies have been used by several authors [e.g. Hall et al. 1981, Raj et al. 1980] to bring the signal which carries the spectroscopic information to a frequency region where the dye laser noise is low.

Shortly after paper VI was published two interesting papers on Doppler-free spectroscopy on hollow-cathode discharges were published by Hannaford and co-workers [Gough and Hannaford 1985, Gough et al. 1985]. Their papers contain information on the hyperfine structure in vanadium as well as other elements and they have also carefully analysed different contributions to the observed linewidth.

B. Lifetime measurements

Lifetime measurements have been performed in papers III, IV and V in this thesis. In all three cases pulsed lasers have been used for two-step excitation of the atoms. For the detection we have collected the fluorescence light emitted at right angles to both the laser beam and the atomic beam.

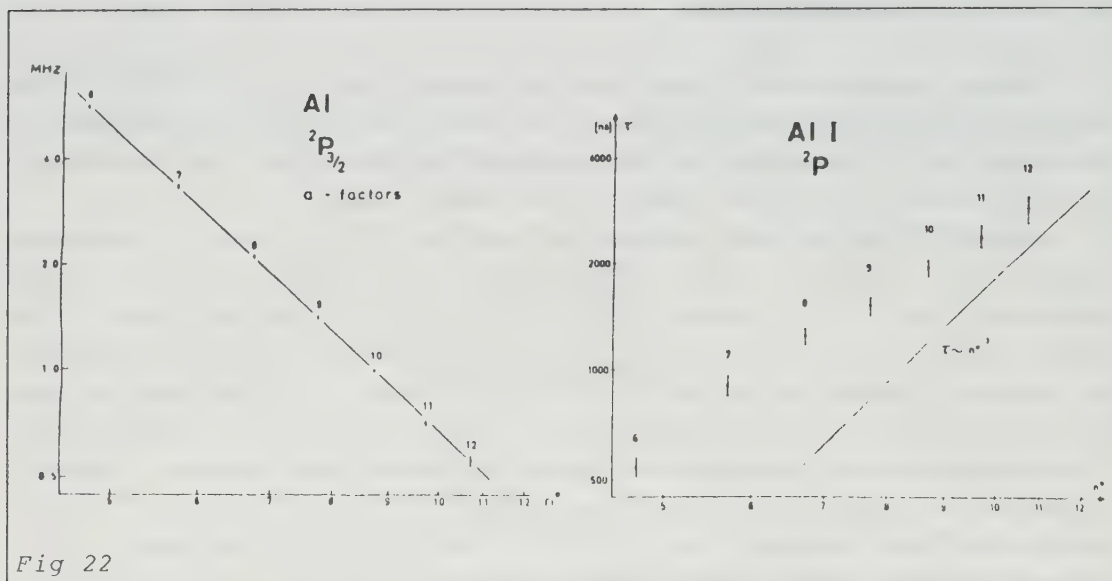
In paper III lifetimes were measured in the $3s^2np\ ^2P_{3/2,1/2}$ ($n=6-12$) sequences of aluminum. These were substantially longer than the lifetimes in the s- and d-sequences [Jönsson and Lundberg 1983]. Thus, as also pointed out in paper III, the measured lifetimes values may be significantly affected by black-body radiation. The measured lifetime values pertain to room temperature. To estimate an upper limit for the lifetimes at zero degrees Kelvin a maximum value for the black-body-induced transition rate need to be assumed. The high- n approximation (chapter V, section A3) is not appropriate for the low n -values in this measurement. Instead we use a black-body transition rate of $10^5\ s^{-1}$, which is about the maximum rate calculated for hydrogen, helium or any of the alkalis [Farley and Wing 1981]. In TABLE II the lifetimes at zero degrees Kelvin, calculated assuming a black-body-induced transition rate of $10^5\ s^{-1}$, are shown together with our values measured at 300 degrees Kelvin.

TABLE II

n	$\tau_{\text{measured}}\ (\mu\text{s})$	$\tau_{\text{upper limit}}\ (\mu\text{s})$
7	0.92	1.01
8	1.25	1.48
9	1.52	1.79
10	1.95	2.42
11	2.41	3.18
12	2.88	4.04

The upper limit lifetimes scale as $\tau(\text{upper limit}) = 21(n^*)^{2.2}$ which is to be compared with $\tau(\text{measured}) = 27(n^*)^{2.0}$ for the lifetime values at room temperature given in paper III. The strong deviation from an $(n^*)^{3.0}$ dependence of the lifetimes in the measured sequence consequently cannot be explained by black-body induced transitions. On the other hand an $(n^*)^{3.0}$ dependence is not necessarily to be expected as the principal quantum numbers are rather low in this investigation.

The lifetimes can be very sensitive to configuration interaction and for these lower states several configurations may contribute. The hyperfine structure which shows a very regular behaviour in the investigated sequence may not be so strongly affected as the lifetimes (while in other cases the effect of configuration interaction on the hyperfine structure can be very strong indeed; section C, this chapter). Thus the regular behaviour of the a-factors is no contradiction to the fact that the lifetimes (whether corrected or not) do not quite follow a straight line in the logarithmic plot (see Fig. 22).



These two logarithmic plots (taken from paper III) show the magnetic dipole interaction constant for the $3s^2np\ ^2P_{3/2}$ series ($n=6-12$) in aluminum (left) and the lifetimes in the same states (right) plotted versus the effective principal quantum number. (The $^2P_{1/2}$ states and the $^2P_{3/2}$ states had the same lifetimes within the measurement accuracy.) While the values for the magnetic dipole interaction constant exactly follow a straight line the lifetimes show a somewhat more irregular behaviour.

In paper IV the main point of interest is the probing of the interaction between the $3s^2nd\ ^1D_2$ sequence and the $3p^2\ ^1D_2$ perturber. An interesting detail here is that the $3p^2\ ^1D_2$ state mixes into the whole $3s^2nd\ ^1D_2$ sequence as well as the adjacent continuum. As the $3p^2\ ^1D_2$ wave function is not localized to any particular state no level has been assigned the $3p^2\ ^1D_2$ label. The lifetime for a particular s- or d-state (here denoted with index j) is related to the oscillator strengths

for the transitions to lower states i by

$$\tau_j = \frac{\epsilon_0 m c g_j}{2\pi e^2 \sum_i \frac{g_i f_{ij}}{(\lambda_{ij})^2}}$$

ϵ_0 = the dielectric constant

$g_j(g_i)$ = the degeneracy of the state $j(i)$

λ_{ij} = the wavelength of the transition between i and j

f_{ij} = the oscillator strength in absorption for the transition from i to j

The summation in the equation above is in principle done over all states below j . However, normally only states with an allowed electric dipole transition to the state j have a non-negligible contribution to the total transition rate. Froese Fisher has calculated the gf values (the oscillator strength in absorption multiplied by the degeneracy of the lower level) for the p-s and p-d transitions in Mg [Froese Fisher 1975(a), Froese Fisher 1975(b)]. To calculate the lifetimes of the d-states the oscillator strength for f-d transitions would also be needed. However for a one-electron system, and often also for other atomic systems, the oscillator strengths for transitions where Δn and Δl have the same sign are much larger than the oscillator strengths for transitions where Δn and Δl have opposite signs [Cowan 1981, p. 429, Bethe and Salpeter 1977, table 14]. Due to this, and the fact that no oscillator strengths were calculated for the f-d transitions, only the p-d transition oscillator strengths were used when calculating the lifetimes for the d-states. Another justification for neglecting the f-d transitions is that the factor λ_{ij} in the equation above will be large for all f-d transitions and their contribution will thus be very small. Also, clearly the strongest contribution to the transition rates from the d-states is from the 3p-nd transitions which possibly indicates that the contributions from the mf-nd transitions may not be very large as the smallest value of m is 4. Finally, the good agreement between the calculated and the measured values indicates that it is reasonable to neglect the f-d transitions when calculating the lifetimes. The very good agreement between the experimental lifetimes and the lifetimes calculated from Froese Fisher's computation is somewhat remarkable, especially since the cancellation effects that occur in the matrix elements between the d- and the p-states make the oscillator strengths quite sensitive to changes in the admixture coefficients. The good agreement implies that oscillator strength (or lifetime) computations can be quite accurately performed for (at least) light elements. The sensitivity to the admixture coefficients indicates that lifetime measurements in some cases may be a sensitive probe for the configuration interaction also for low-lying states. However, this kind of interaction demands more elaborate calculations in order to extract information about the interaction than in e.g. the case where a short-lived state belonging to a doubly excited configuration interacts with long-lived states in a Rydberg sequence.

As mentioned above it is of special interest to investigate the light elements since theoretical calculations often can be performed quite accurately for such elements. Unfortunately it is difficult to use laser excitation for preparing atoms which belong to elements in the second row of the periodic system in excited states since mostly quite high energies (short wavelengths) are needed to reach these states. It can also be difficult to create free atoms of these elements under circumstances where measurements of the atomic properties can be reliably performed. These complications have, to some extent, been overcome for oxygen where lifetime measurements have been performed for the lower members in the $2p^3ns\ ^3S$ and $2p^3nd\ ^3D$ sequences, as described in paper V. In this investigation free oxygen atoms were created by photodissociation of NO_2 . By using non-resonant two-photon absorption of two UV $\lambda = 226\text{ nm}$ photons the energy gap between the $2p^4\ ^3P$ ground state and the $2p^33p\ ^3P$ state could be bridged. From the $2p^33p\ ^3P$ state all $2p^3ns\ ^3S$ and $2p^3nd\ ^3D$ states with $n > 5$ are then accessible using a single visible photon for excitation.

To be able to judge the prospects for the future for this technique we made some estimates of the percentage nitrogen dioxide molecules dissociated and how many of the created oxygen atoms that were excited to the $3p\ ^3P$ state. Some calculations were also carried out in order to assure that radiative trapping could be neglected in the measurements. Only the results of these calculations were given in the paper but they will be described here in somewhat more detail.

Measurements were made at pressures ranging from about 100 Pa down to 1 Pa. Stern-Vollmer plots were made to separate the spontaneous decay from the collision-induced decay. (1 Pa NO_2 corresponds to $\sim 3 \times 10^{14}$ molecules/ cm^3 .) The pulse energy at 226 nm was about 1 mJ which corresponds to about 10^{15} photons/pulse ($=N_0$). The number of absorbed photons along a distance ℓ at molecular density M is

$$N_0(1-\exp(-kM\ell))$$

k is the absorption coefficient for NO_2 at $\lambda = 226$ ($k = 3 \times 10^{-19}$ molecules $^{-1}$ cm $^{-1}$ [Okabe 1978, p. 228]). At a pressure of 1 Pa the argument in the exponential will be very small if $\ell < 1\text{ m}$ so the number of absorbed photons can be approximated by

$$N_0 k M \ell \tag{23}$$

At photon energies below 244 nm there is sufficient energy to leave the oxygen atom formed in the dissociation process in the metastable $2p^4\ ^1D$ state at about 15000 cm^{-1} above the ground state. At 226 nm roughly 50% of the dissociated atoms will be left in this state instead of in the ground state [Nakayama *et al.* 1959]. Another potential disadvantage of using this short-wavelength radiation to dissociate the molecules is that the NO_2 absorption coefficient has its maximum at 400 nm where it is about twice as large as it is at 226 nm. Nevertheless it turns out that the energy at 226 nm is sufficient for both dissociating the molecules and exciting the oxygen atoms. To estimate excitation rates and other quantities it is necessary to know the beam diameter at focus. Calculating the beam waist is difficult since we do not know the mathematical description of the laser mode. However, mathematical

descriptions of non-gaussian laser beams exist [Phillips and Andrews 1983] and attempts have been made to use this to describe the mode of a YAG pumped dye laser [Greenhalgh and Whittley 1985]. To calculate the beam waist, lens aberrations would also need to be taken into account. In paper V it was assumed that the laser beam waist would be about $100\text{ }\mu\text{m}$. It was later measured by moving a razor blade mounted on a micrometer translator through the beam. This gave a diameter of $70\text{ }\mu\text{m}$ at the focal point and $140\text{ }\mu\text{m}$ 3 mm from the focal point. A 6 mm long section of the beam was imaged on a horizontal slit in front of the photomultiplier. (The volume in the part of the laser beam imaged on the photomultiplier is then about $2 \times 10^{-4}\text{ cm}^3$.) At 1 Pa this volume contains about $6 \times 10^{10}\text{ NO}_2$ molecules. Starting with 10^{15} photons we see from Eq. 23 that about 6×10^{10} photons will be absorbed in 0.6 cm .

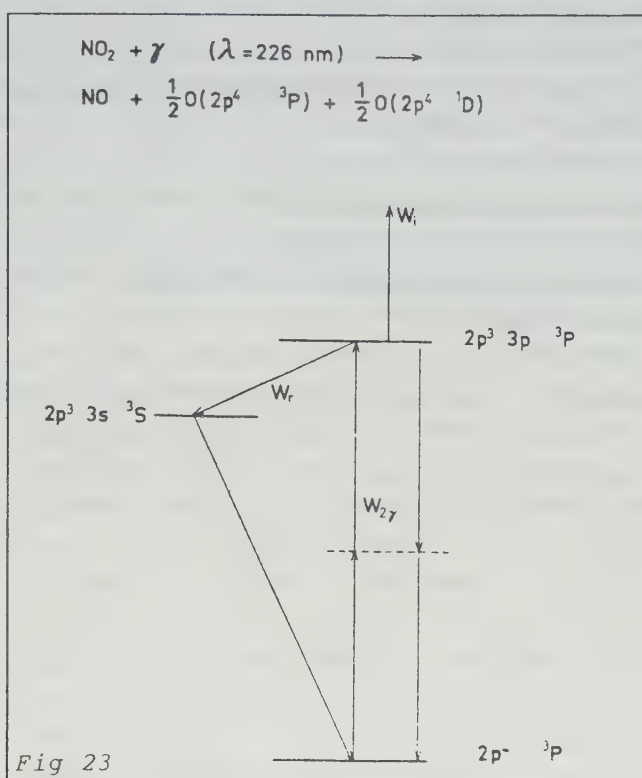


Fig 23

The processes indicated in the diagram above photodissociation, two-photon absorption, stimulated two-photon emission, photoionization and radiative decay of the $3p\ ^3P$ state, have been included in the rate equation model.

However, as the NO_2 molecule density M in the focal region changes, the absorption changes. To make a better estimate of the population in the various states after the laser pulse, I will perform a brief calculation based on the the following assumptions. The laser pulse is 6 ns long and its intensity is uniformly distributed over time, and over a circular area with the diameter measured above (let us chose $100\text{ }\mu\text{m}$). The influence of the laser pulse on the atomic population is sufficiently strong for collisional processes to be neglected. This seems perfectly acceptable at a pressure of one Pa with the quenching cross sections estimated from

our results in paper V. The quenching rate at these pressures is about a factor of 1000 smaller than the transition rates due to radiative processes. The processes depicted in Fig. 23 has been included in the calculations. The time for radiative decay from the $2p^3 3p^3 P$ to the $2p^4^3 P$ state via the $3s^3 S$ state has been approximated by the time for radiative decay from $3p^3 P$ to $3s^3 S$. I.e. the lifetime for the $3s^3 S$ state (about 2 ns [Brooks et al. 1977]) has been neglected in comparison with the lifetime of the $3p^3 P$ state (about 40 ns).

$W_{2\gamma}$ = the two-photon absorption rate.

$W_{2\gamma} = g\sigma F^2$

F = the flux, i.e. the number of photons/(area x second)

σ = the two-photon absorption cross section ($\approx 7 \times 10^{-36} \text{ cm}^4$ [Omidvar 1980(a), Pindzola 1978])

g = a linewidth factor which is discussed in e.g. Ref. [McIlrath et al. 1979]. In this case g is inversely proportional to the laser linewidth $g = (\pi^2 \delta\nu)^{-1}$

$\delta\nu = 30 \text{ GHz}$

W_r = the spontaneous radiative decay rate

$W_r = 1/\tau$

τ = the natural radiative lifetime for the $2p^3 3p^3 P$ state

W_i = the photoionization rate

$W_i = \sigma_i F$

σ_i = the photoionization cross section ($\approx 10^{-19} \text{ cm}^2$ [Omidvar 1980(b)])

The following rate equations are used

$$dN_{\text{NO}_2}/dt = - N_0 k l (N_{\text{NO}_2}/V) \quad (24)$$

$$dN_{2p}/dt = -(1/2)(dN_{\text{NO}_2}/dt) - W_{2\gamma}(N_{2p} - N_{3p}) + W_r N_{3p} \quad (25)$$

$$dN_{3p}/dt = W_{2\gamma}(N_{2p} - N_{3p}) - (W_r + W_i)N_{3p} \quad (26)$$

$$dN_{\text{O}^+}/dt = W_i N_{3p} \quad (27)$$

On the left-hand side in Eqs. 24-27 we have the changes per unit time in the number of NO_2 molecules, $2p^4^3 P$ oxygen atoms, $2p^3 3p^3 P$ oxygen atoms and oxygen ions respectively. Direct three-photon photoionization from the $2p^4^3 P$ state and ion-electron recombination has been neglected. The validity of these approximations has been discussed in a similar approach by Omidvar [Omidvar 1980(b)]. However, no dissociation process was included in his analysis. It has here also been assumed that all dissociated oxygen atoms are created in the $J = 2$ level in the ground state. Eq. 24 above is basically the same as Eq. 23 but a factor $1/V$, where V is the volume of the part of the laser beam imaged on the photomultiplier tube has been included on the right-hand side. The initial conditions are

$$N_{\text{NO}_2}(t=0) = 6 \times 10^{10}$$

$$N_{2p}(t=0) = 0$$

$$dN_{2p}/dt(t=0) = (1/2)N_0 k \lambda N_{\text{NO}_2}(t=0)/V$$

$$N_{3p}(t=0) = 0$$

$$dN_{3p}/dt(t=0) = 0$$

$$N_{\text{O}^+}(t=0) = 0$$

The level $2p^4\ ^3P$ is populated through photodissociation of NO_2 molecules (of which half are left in the $2p^4\ ^1D$ state) and radiative decay and stimulated two-photon emission from the $2p^3 3p\ ^3P$ state, and it is depopulated by two-photon absorption to the $2p^3 3p\ ^3P$ state. The $2p^3 3p\ ^3P$ state is populated by two-photon absorption from the ground state and deexcited by spontaneous and stimulated emission to the $3s\ ^3S$ state and the ground state, respectively, and it is also depopulated by photoionization. Finally, the oxygen ions are assumed to be created by one-photon ionization from the $3p$ state only. Solving Eqs. 24–27 with the initial conditions above for a laser pulse of 6 ns duration and a laser flux of 2.4×10^{27} photons $\text{cm}^{-2} \text{s}^{-1}$ results in roughly 25% of the initial NO_2 molecules being finally in the oxygen ground state. The population of the $3p\ ^3P$ state is about 20% of the population in the oxygen ground state and the number of oxygen ions is about 15% of the ground state population. The two-photon absorption cross section used for the calculation have not been multiplied with the second-order correlation function of the laser field. I.e., we have implicitly assumed that the second-order correlation function is equal to one. This would be the case for a perfectly coherent laser beam. However a YAG laser or a YAG pumped dye laser is generally far from a perfectly coherent light source and this is especially the case if frequency-doubled and frequency-mixed light is used [Dutta 1979]. Very recently Bamford, Jusinski and Bischel [Bamford et al. to be published] have experimentally measured the two-photon absorption and photoionization cross sections used in the calculations above. Their results indicate that if, as in our paper, frequency mixing is used to produce the 226 nm wavelength the theoretical value for the two-photon absorption cross section need to be multiplied with a factor of four to account for the photon statistics of the exciting field. Alternatively, if Raman shifting is employed for producing the 226 nm radiation the cross section should be multiplied with a factor of two. This latter case would correspond to chaotic photon statistics which often is assumed for this kind of lasers. Their value for the two-photon absorption cross section itself is also slightly higher than the theoretical values (Omidvar gives a new value for the two-photon absorption cross section in an errata [Omidvar 1984] to his previous paper [Omidvar 1980 (a)]). Not only the effective cross section for the two-photon absorption (in this case the effective cross section means the theoretical cross section multiplied with the correlation function for the exciting light), but also the photoionization cross section obtained by Bamford et al. was about a factor of five larger than the

values used in the calculations above. The results of Bamford et al. indicate that the photoionization of oxygen atoms in the $3p\ ^3P$ state might be a more serious problem than our calculations show. However, although absolute values cannot be given, (the knowledge of the photon statistics of our laser as well as theirs is insufficient) it still seems reasonable that the first step laser pulse will produce an appreciable amount of oxygen atoms in the $3p\ ^3P$ state. These atoms can then be further excited.

Another relevant question is if the lifetime measurements can be affected by radiation trapping. The risk can be severe since the studied states have quite strong allowed transitions to the ground state. Following e.g. [Mitchell and Zemansky 1971, chapter 3, Jenkins 1981] the intensity transmitted through an atmosphere with a certain concentration of oxygen atoms can be written

$$I = I_0 \exp\{-\sigma(\lambda)[O(^3P_J)]_A \ell\}$$

$\sigma(\lambda)$ = the absorption cross section ℓ = the absorption path length
 $[O(^3P_J)]_A$ = the concentration of ground state 3P_J atoms at temperature A

In thermal equilibrium at room temperature about 75 % of the $2p\ ^3P$ atoms would be in the 3P_2 state (at a higher temperature the population would be lower so this represents a worse situation), but as we do not know in which of the fine structure levels the oxygen atoms are formed after the photodissociation we might assume that all are in the 3P_2 state. For the absorption cross section we have

$$\sigma(\lambda) = \frac{2\lambda_0^2 e^2 f \sqrt{\pi \ln 2}}{4\pi\epsilon_0 c^2 \Delta\lambda_D} \exp - \left[\frac{2(\lambda - \lambda_0)^2 \sqrt{\ln 2}}{\Delta\lambda_D} \right]^2$$

λ_0 = the resonance wavelength for transitions from s- and d-states to the ground state

f = the oscillator strength for the transition

$\Delta\lambda_D = 2(2R \ln 2)^{1/2} \lambda_0 (T_A/M)^{1/2} / c$ = the Doppler width

R = the gas constant

T_A = the temperature

M = the mole mass

For the reabsorption of the emitted photons to be negligible

$$\sigma(\lambda_0)[O(^3P_2)]_A \ell \ll 1$$

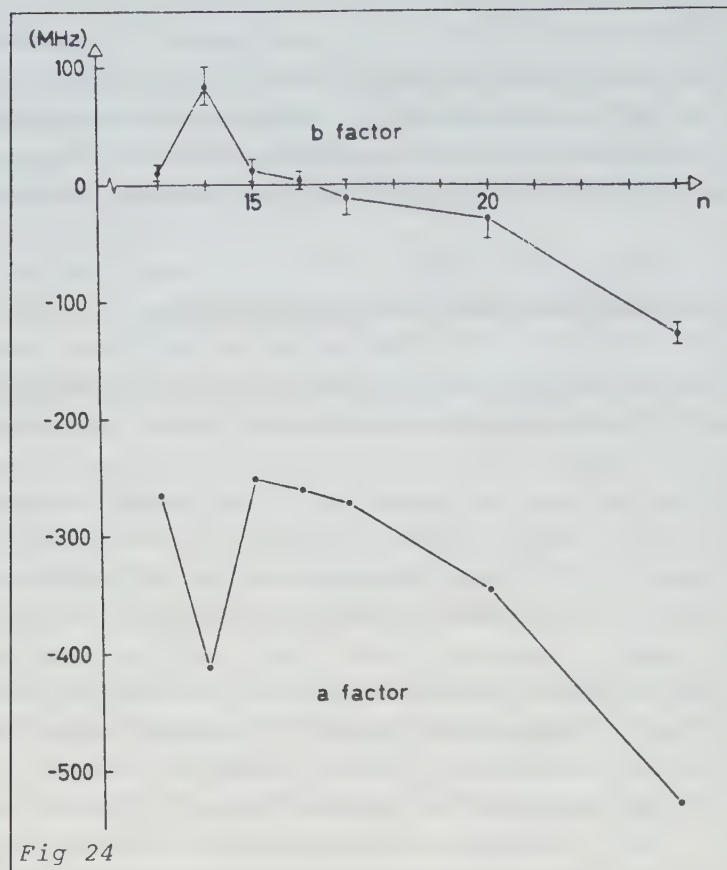
is an appropriate condition. At 1 Pa the ground state oxygen atom concentration $[O(^3P_2)] = 3 \times 10^{14} \times 1/4 \text{ cm}^{-3}$ after the laser pulse. The highest oscillator strength connecting the levels investigated and the ground state was $f = 0.015$ [Pradhan and Saraph 1977]. This gives

$$\lambda \ll 0.25 \text{ cm}$$

as the condition for trapping to be negligible. With a beam diameter ranging from 70 to 140 μm we are on the safe side in our measurements. It is, however, worth noticing that if a flow discharge were used instead of photodissociation to produce the oxygen atoms the problem of trapping would be considerably more difficult to handle.

C. Doppler-free measurements on atomic beams

In paper I the hyperfine structure and isotope shifts were measured in the Ba $6snd\ ^1D_2$ sequence for principal quantum numbers $n = 13-17, 20, 24$. For perfect LS coupling the magnetic dipole part of the hyperfine structure in the $6snd\ ^1D_2$ sequence would arise only from the orbital part of the nd -electron wave function. This would be very small for Rydberg states since the orbital contribution (and the spin-dipole one) goes as $\langle r^{-3} \rangle$ which is proportional to $(n^*)^{-3}$. In the absence of a configuration interaction an increase in the hyperfine structure for higher Rydberg states would then reflect a transition from LS to jj coupling. This would give a pronounced hyperfine structure due to the Fermi contact interaction from the inner $6s$ electron. For this configuration ($6snd$) jj coupling would, to a good approximation, give an a -factor of $a_{6s}/4$ [Kopfermann 1958, p. 143], where $a_{6s}(l+1/2)$ is the splitting between the hyperfine levels in the Ba^+ ion. ($a_{6s} \approx 4$ GHz [Becker et al. 1968]). However, as is normally the case for the alkaline earth Rydberg sequences the Ba $6snd\ ^1D_2$ sequence is perturbed by doubly excited states. Referring to Fig. 24, which is the same as Fig. 3 in paper I, one can see a localized perturbation of the hyperfine structure at $n = 14$ due to the interaction with the doubly excited $5d7d\ ^3F_2$ state. This interaction had previously been studied in energy level [Aymar et al. 1978], g_j -factor [Grafström et al. 1982] and lifetime measurements [Bhatia et al. 1981, Gallagher et al. 1981, Aymar et al. 1981]. Our paper on the hyperfine structure and isotopic shift was unfortunately misplaced at the editorial office. Due to the resulting several months' delay it was published at about the same time as the very thorough hyperfine and isotope-shift investigations of the $nd\ ^1D_2$ sequence, including the higher members, by Rinneberg and Neukammer in Berlin [Rinneberg and Neukammer 1982(b), Neukammer and Rinneberg 1982, Rinneberg and Neukammer 1983]. For these higher states the hyperfine splitting increases and the magnetic dipole interaction constants show a dispersion-shaped resonance due to the admixture of triplet character into the singlet series induced by the interaction between the $5d7d\ ^1D_2$ state and the singlet and triplet series. The interaction of a discrete (autoionizing) state with two interacting continua has been treated by Fano [Fano 1961] and the connection between this case and the case of the perturbation of a short-lived excited state in a Rydberg series is outlined in an appendix to this paper. This and a later paper [Fano and Cooper 1965] on the same subject were in this respect the predecessors to the papers by Fano and co-workers on MQDT [Lu and Fano 1970, Fano 1970, Lu 1971, Lee and Lu 1973].



The values for the magnetic dipole interaction constants (a) and the electric quadrupole interaction constants (b) in the $6snd\ ^1D_2$ sequence in barium ($n=13-17, 20, 24$) are plotted versus the effective principal quantum number. The perturbation caused by the $5d7d\ ^3F_2$ state at $n=14$ can be seen in the plot.

The hyperfine interaction which arises almost exclusively from the Fermi contact interaction between the nucleus and the $6s$ electron is described by a Hamiltonian [Kopfermann 1958, p. 140]

$$H_{\text{int}} = a_{6s} \mathbf{I} \cdot \mathbf{s}_{6s} = a_{6s} (\mathbf{I} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{\Sigma})/2$$

$$\mathbf{S} = \mathbf{s}_{6s} + \mathbf{s}_{\text{nd}}$$

$$\mathbf{\Sigma} = \mathbf{s}_{6s} - \mathbf{s}_{\text{nd}}$$

where the last term will mix the singlet and the triplet series. This mixing, induced by the Fermi contact interaction, is denoted hyperfine-induced singlet-triplet mixing [Liao et al. 1980, Freeman et al. 1980, Matthias et al. 1983, Rinneberg to appear]. For sufficiently large n the Fermi contact interaction will be comparable to the spin-orbit interaction and it then needs to be included in the Hamiltonian for calculating the energy levels. This will shift the singlet levels

for the isotopes with non-zero nuclear spin. Such a case is discussed by Beigang and Timmermann [Beigang and Timmermann 1982] for the msns $^1S_0, ^3S_1$ series in the alkaline earths and extended for Ba [Rinneberg et al. 1982] to incorporate a doubly excited perturber state simultaneously interacting with the singlet and triplet series. For the 6snd 1D_2 series in Ba the situation is even more complicated since there are several doubly excited states which need to be included in the modelling.

In paper III hyperfine structure measurements using quantum beat spectroscopy in the $6s^2np \ ^2P_{3/2}$ states ($n = 6-12$) were performed as well as lifetime measurements. For the states $n = 6-9$ not only the magnetic dipole interaction constants (a) but also the electric quadrupole interaction constants (b) were determined. For an alkali atom this second quantity is connected to the nuclear quadrupole moment (Q) by ([Kopfermann 1958, p. 154])

$$b = (e^2/4\pi\epsilon_0)(2j-1)/(2j+2)Q\langle r^{-3} \rangle_q R_r(\ell, j)$$

$R_r(\ell, j)$ = is a relativistic correction factor ($<1\%$ in this case)

ℓ = the orbital quantum number of the outer electron

ϵ_0 = the permittivity of free space

$\langle r^{-3} \rangle_q$ = is the expectation value of $1/r^3$

This is expressed in Ref. [Belin et al. 1976(a)] as

$$Q(\text{in barn}) = 1.06395 \times 10^{-2} \ b_{3/2}/\langle a_0^3/r^3 \rangle \quad (28)$$

where $b_{3/2}$ is in MHz and a_0 is the Bohr radius. In the non-relativistic limit the expectation value for the denominator can be obtained from the fine structure splitting δW

$$\delta W = \mu_0/(4\pi a_0^3) 2\mu_B^2 (\ell+1/2) Z_i H_r(\ell, Z_i) \langle a_0^3/r^3 \rangle \quad (29)$$

$\mu_B = eh/(4\pi m)$ = the Bohr magneton

μ_0 = the permittivity of free space

$Z_i = Z - 4$ for p-electrons [Belin et al. 1976(b)]

Z = the nuclear charge

$H_r(\ell, Z_i)$ = a relativistic correction factor which can be obtained from Ref. [Kopfermann, table 8].

All quantities are in SI units. Solving $\langle a_0^3/r^3 \rangle$ from Eq. 29 and inserting in Eq. 28 gives the quadrupole moment. To check the consistency of the values measured for the b-factors this procedure was used in paper III to calculate the quadrupole moment. The results ($Q \approx 0.14$ barn) obtained were internally consistent and quite reasonable (Ref. [Kopfermann, table 62a] gives 0.149 barn). If the a-factors were measured also for the $^2P_{1/2}$ states, these could be used instead of the fine structure splittings for calculating a quadrupole moment from the a-factors for the $^2P_{3/2}$ states. Such a procedure was used for the alkalis in e.g. Refs. [Belin et al. 1976(a), Belin et al. 1976(b)] and have been shown to work well also for the 2P states in group III elements [Jiang et al. 1982, Jönsson

et al. 1983, *Belfrage et al.* 1984] although later many-body calculations [Jönsson *et al.* 1985] have shown that core polarization as well as correlation effects are strong in the $np\ ^2P_{3/2}$ states in the group III elements.

VII CONCLUSIONS

Several types of saturation spectroscopy techniques have been intercompared with regard to their potential for Doppler-free measurements in a hollow-cathode discharge. Cross-over resonances, line shapes, velocity-changing collisions, choice of modulation frequency and other questions relevant to this measurement situation have been discussed. The techniques have been compared in conjunction with Doppler-free measurements on neon, molybdenum and vanadium and new data on the hyperfine structure in vanadium have been presented.

Lifetime measurements have been performed in Rydberg sequences using pulsed laser excitation. Lifetime measurements in the $nd\ ^1D_2$ sequence in magnesium have shown that excited state lifetimes can be a sensitive test for theoretical computations. The measurements of excited state lifetimes in the $ns\ ^3S$ and $nd\ ^3D$ sequences in oxygen demonstrate that pulsed laser excitation can be used for measuring excited state lifetimes in most elements in the second row of the periodic system. The ground state oxygen atoms were here produced by laser photodissociation of nitrogen dioxide.

The hyperfine structure in the $np\ ^2P_{3/2}$ sequence ($n=6-12$) in aluminum has been determined using pulsed laser excitation and quantum-beat spectroscopy, and the hyperfine structure and isotope shifts in the barium $nd\ ^1D_2$ sequence ($n=13-17,20,24$) have been measured using continuous-wave dye lasers for two-step excitation of a collimated atomic beam.

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